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A Study of Calcium Carbonate Crystal Growth in the Presence of a Calcium Complexing Agent

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A STUDY OF CALCIUM CARBONATE CRYSTAL GROWTH IN THE PRESENCE OF A CALCIUM COMPLEXING AGENT

A thesis submitted by

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SUMMARY

Temperature-sensitive calcium organic complexes are believed to be essential in the mechanism of black liquor evaporator scaling. Therefore, in the present study, the effect of a calcium complexing agent, iminodiacetic acid, on the rate of calcite growth was studied. Calcite growth trials were conducted at 25, 35, and 45°C and at a pH of approximately 10. In each trial seed crystals were introduced to a metastable supersaturated solution, and changes in the ionic content of the solution were monitored using conductivity and pH measurements.

The pH of growth solutions prepared with equal chemical concentrations was determined to be temperature dependent. The lower pH and the lower stability of the calcium-iminodiacetic acid complex led to an increased availability of ionic calcium in the 45°C solution. This result supported the hypothesis of Grace and Frederick that heating a system containing calcium, carbonate, and a complexing agent causes a shift from complexed calcium to ionic (or scalable) calcium. The conclusion of Westervelt regarding the importance of pH was also verified.

It was also determined that the presence of 3.33 moles of iminodiacetic acid (IDA) per mole of calcium in the solution reduced the growth rate constant of calcite at all temperatures investigated. Larger amounts of IDA, e.g., 6.67 moles of IDA (or more) per mole of calcium, inhibited growth completely. The concentration of IDA needed for growth inhibition is not predicted solely by the complexation process. To explain the additional role of IDA molecules in the calcite growth reaction, a mechanism has been proposed. An adsorbed monolayer of hydrated ions surrounding each crystal is postulated. Calcium and carbonate ions colliding with the monolayer at an active growth site may enter the monolayer by causing dehydration of the underlying ions. The entry of the dehydrated ions into the crystal lattice constitutes crystal growth. However, the presence of ions of iminodiacetic acid in the monolayer blocks active growth sites since the iminodiacetic acid cannot enter the crystal lattice. It is the blocking action of the

iminodiacetate ions which increases the effectiveness with which IDA inhibits calcite crystal growth. This mechanism was previously proposed by Davies and Jones in their study of silver chloride crystal growth. Based on the proposed mechanism, it is suggested that scaling is not only a function of available calcium, but also depends on the blocking action of lignin fragments present in the black liquor.

INTRODUCTION

PERSPECTIVE

Scaling is the deposition of material on heat transfer surfaces. It arises from the creation of a supersaturation potential by evaporation, cooling, or mixing. Scaling can be a major problem in cooling water systems, steam generation, and drinking water supply systems (1). In the pulp and paper industry, scale deposits are most notable in kraft digesters (2,3) and black liquor evaporators (4). Although scale compositions vary from mill to mill, the scales are usually composed primarily of calcium carbonate (5).

Calcium carbonate scale specimens from a kraft digester have been examined by Hartler and Libert (3). Electron microscopy indicated that the scale was composed of large crystals. Accordingly, Hartler and Libert concluded that the scale was formed by continuous crystal growth and not by agglomeration of the small entrained calcium carbonate particles.

Grace and Frederick (4) first examined scaling as a function of calcium carbonate solubility. Analyzing black liquor samples from several mills, they found that the carbonate concentration was much higher than the calcium concentration. Therefore, they concluded that the supersaturation potential of calcium carbonate is determined by the concentration of calcium. However, the total calcium content of the solution phase of the black liquor was determined to be several orders of magnitude larger than the saturation concentration of calcium. Therefore, Grace and Frederick proposed that some of the calcium may be bound by other constituents of the black liquor such as the alkali lignin, the hydroxy acids, and/or the extractives. This would lead to an ionic calcium content much lower than the total calcium content.

Grace and Frederick (4) also studied the mechanism of scaling using model liquors in a laboratory scaling apparatus. In an inorganic model liquor containing calcium only as calcium oxalate, no scale formed on an electrically heated test strip. Therefore, the change in the relative solubilities of calcium oxalate and calcium carbonate with temperature is not sufficient for calcium oxalate to act as a source of ionic calcium. However, when a portion of the calcium was complexed with an aromatic compound with adjacent hydroxyl groups, appreciable scale was formed. From these studies, Grace and Frederick (4) proposed that lignin fragments formed during pulping complex with the calcium in black liquor. They further postulated that at the elevated temperatures of evaporator tube walls, the complexes dissociated to release ionic calcium which could then combine with the abundant carbonate ion to form scale. This scaling mechanism is depicted in Fig. 1.

Westervelt (6) studied the structure and stability of a catechol derivative complex with calcium to model the lignin fragments. He showed the distribution of calcium to be a complex function of temperature, base concentration, and ionic strength. This contradicted the straightforward relationship involving only temperature and chelate stability proposed by Grace and Frederick (4).

Grace and Frederick (4) assumed calcium-lignin fragment complexes function solely as a reservoir of free ionic calcium. They made no assumptions concerning the effect of the lignin fragments on the growth rate of scale. Therefore, the current investigation was designed to study the growth of calcium carbonate crystals in the presence of a calcium complexing agent. In particular, the effect of the complexing agent on the rate of calcite growth will be examined.

THESIS OBJECTIVES

The purpose of this study was to determine the effect of a calcium complexing agent in supersaturated solution on the kinetics of calcite growth and to apply the

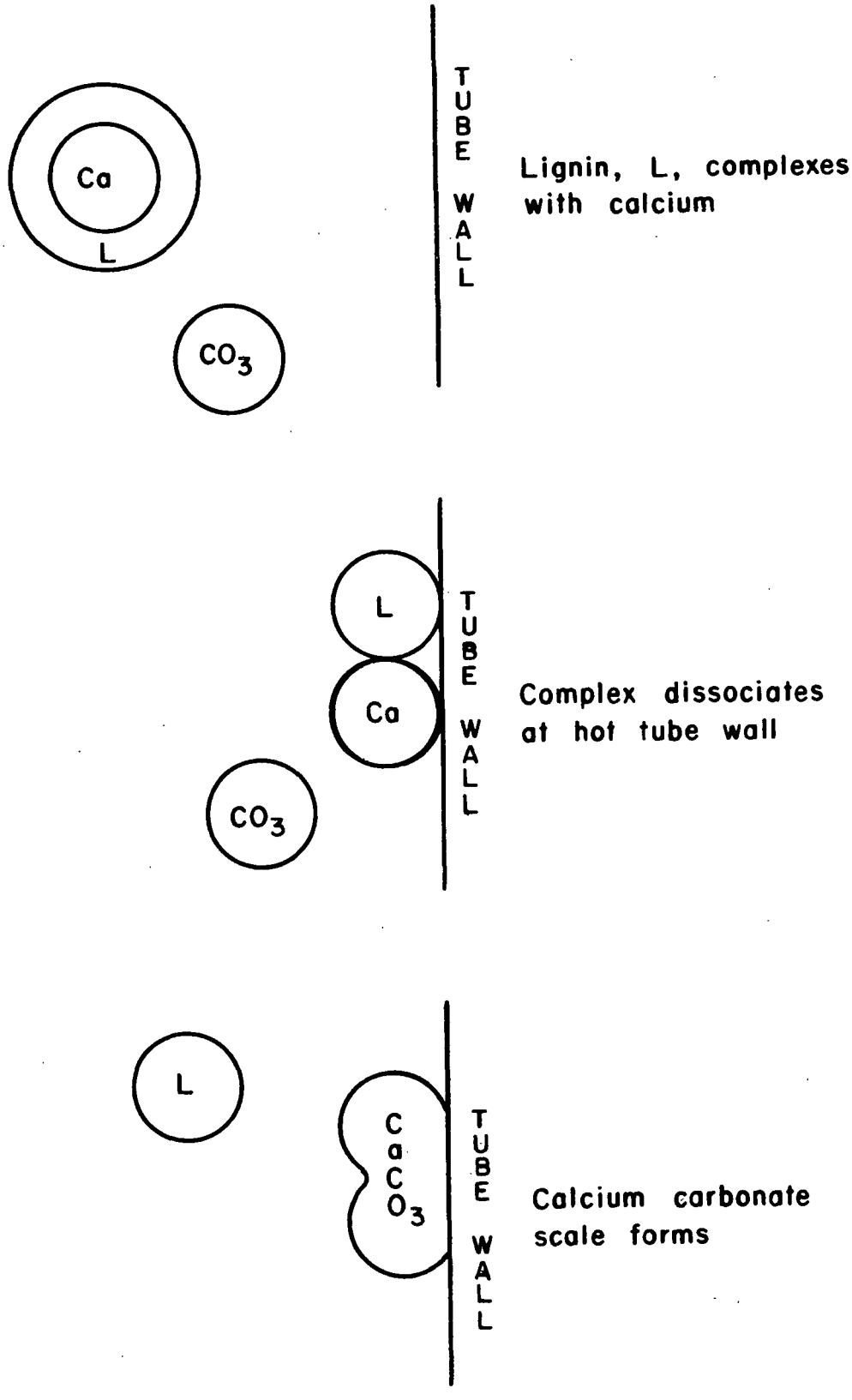


Figure 1. Grace and Frederick (4) Calcium Carbonate Scaling Mechanism

experimental findings to a better understanding of the process of scaling in kraft black liquor evaporators.

The first objective of the study was to determine the equivalent conductance at infinite dilution for nitrate, hydroxide, bicarbonate, carbonate, and iminodiacetate ions at 25, 35, and 45°C, so conductivity measurements could be used to follow crystal growth.

The second objective of the study was to establish the affinity of the complexing agent for calcium by determining the stability constants of the complex at 25, 35, and 45°C.

The third objective was to illuminate the crystal growth behavior changes caused by the presence of the complexing agent in the growth solution.

CRYSTALLIZATION - THEORY

Crystallization is the organization of matter into solids of well-defined shapes. The crystals may form from a vapor, from a liquid melt, or from a liquid solution. The crystal formation process involves two distinct steps, nucleation and growth. Nucleation is the initial clustering or joining of the molecules. Growth is the process by which additional molecules are added to the crystal lattice. When nucleation and growth occur simultaneously to produce crystals large enough to settle out of suspension, the crystallization process is termed spontaneous precipitation.

In a solution, supersaturation is the driving force for each crystallization step. Cooling a solution, evaporating the solvent, or mixing two solutions will establish one of two phases of supersaturation, the metastable or the labile, as shown in Fig. 2. In the metastable phase spontaneous nucleation does not occur. The addition of solute crystals will, however, result in growth of those seed

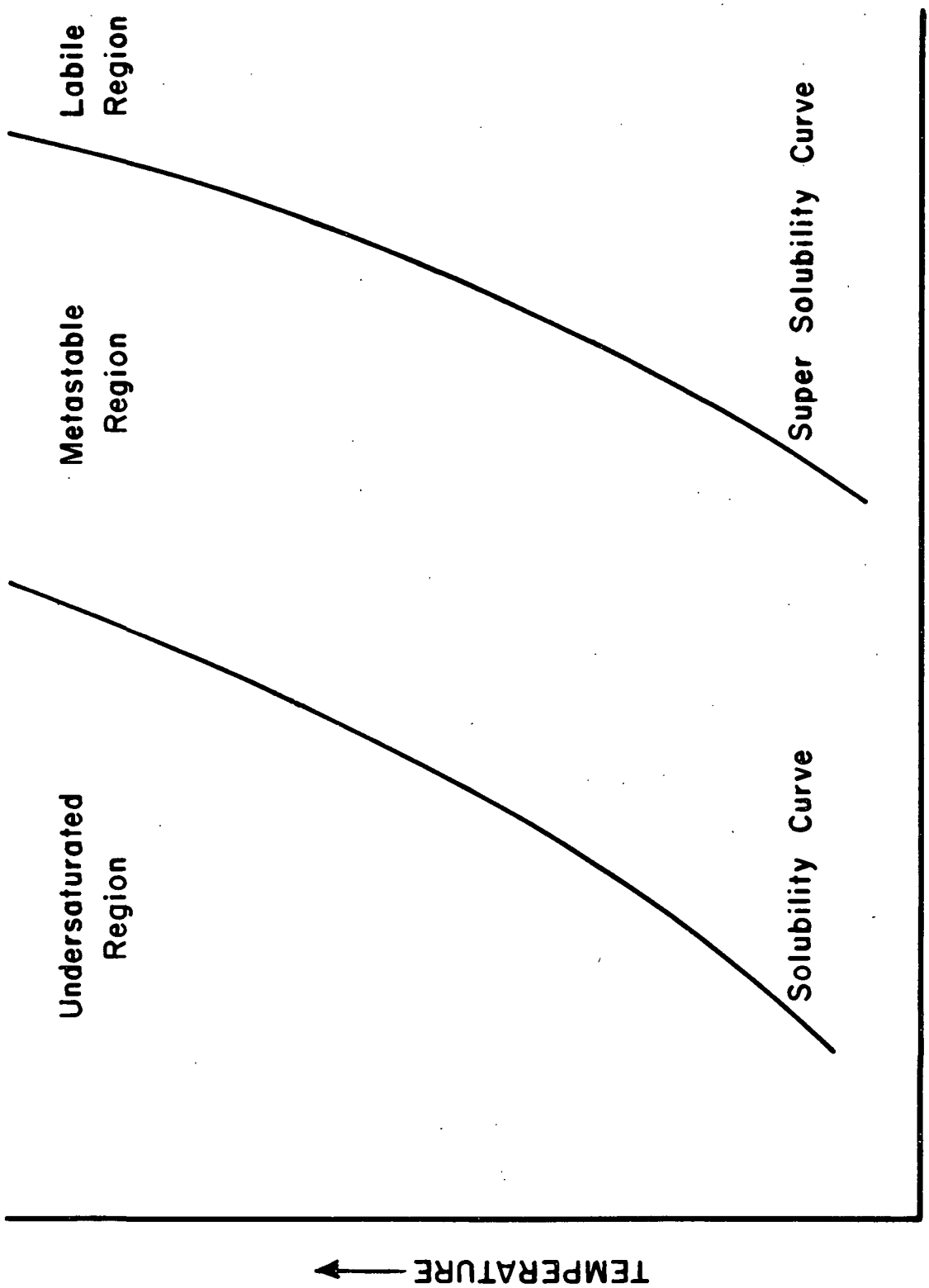


Figure 2. Supersaturation Phases of a Typical Inorganic Salt

crystals. By contrast, in the labile zone, both spontaneous nucleation and growth occur, with or without the addition of seed crystals. Although supersaturation is the driving force for crystallization, nucleation and crystal growth occur at distinct rates (7).

Nucleation

Two forms of nucleation may occur in solution, homogeneous nucleation and heterogeneous nucleation. In homogeneous nucleation, Brownian motion leads to spontaneous orientation and aggregation of solute molecules. The short-lived clusters may then grow to become embryos of definite identity and boundaries. An embryo which attains thermodynamic equilibrium with the solution is a crystal nucleus (7,8). The degree of supersaturation present in the solution will determine the number of embryos which will become nuclei and thus the homogeneous nucleation rate. However, large degrees of supersaturation are required to generate a measurable homogeneous nucleation rate. A much lower degree of supersaturation is necessary to generate a measurable rate if heterogeneous nucleation occurs.

Heterogeneous nucleation differs from homogeneous nucleation in that a solid particle or particles are added to the supersaturated solution. The particle may be a piece of dust, an irregularity in the container surface, or a solute crystal. The particle, if it is wetted by the solution, reduces the energy required to form stable nuclei. Therefore, a lower degree of supersaturation leads to a measurable nucleation rate.

Crystal Growth

It is believed that crystals grow layer by layer, with each layer starting from a two-dimensional nucleus. Once the nucleus attaches to the crystal face, growth by completion of the layer occurs rapidly. This two-dimensional theory predicts that growth starts only when the degree of supersaturation is sufficient to generate a

constant supply of two-dimensional nuclei (7). Actual experiments do not exhibit the predicted lag in growth rate. The difference between theory and experiment is explained by dislocations in the shear plane perpendicular to the crystal surface. The dislocations act as two-dimensional nuclei and lead to the observed linear dependence of growth rate on supersaturation (7,9).

CRYSTALLIZATION - LITERATURE REVIEW

Calcium carbonate crystallization was first studied by following spontaneous precipitation reactions (10,11). Kitano (10) studied the influence of various inorganic ions on the formation of the several polymorphic forms of calcium carbonate. Calcium carbonate can be precipitated as rhombic calcite, needlelike aragonite, or spherulitic vaterite in the laboratory. Calcite, however, is the only thermodynamically stable form of pure calcium carbonate (12). Kitano (10) estimated the rate of calcium carbonate precipitation from pH and total calcium measurements in portions of the supernatant. In addition, Kitano used x-ray diffraction of the precipitate to determine the crystal forms present. Kitano did not, however, form any definite conclusions regarding the mechanism leading to the calcite, aragonite, and vaterite crystal forms. Packter (11) studied the spontaneous precipitation of calcium carbonate while investigating calcium, strontium, barium, and lead carbonates, phosphates, sulfates, chromates, and molybdates. He used assumptions of 1) homogeneous nucleation and 2) simultaneous nucleation and growth to separate the nucleation and growth steps.

Nancollas and Purdie (13) have criticized the assumption of homogeneous nucleation in spontaneous precipitations. They expressed doubt that any practical medium of precipitation could be sufficiently free from available sites to preclude the possibility of induced nucleation. In particular, Nancollas and Purdie noted that reagent impurities and solution contact with container surfaces will lead to

variations in the size and size distribution of the crystals formed in spontaneous precipitation experiments.

Davies and coworkers (14,15) studied crystal growth by adding seed crystals to metastable supersaturated solutions. Under this condition, only crystal growth occurs. Davies used conductivity measurements to follow solution changes and found the rate of growth proportional to the total crystal surface present.

Nancollas and Reddy (16) applied the technique of seeding supersaturated solutions to study the growth of the calcite form of calcium carbonate. They measured calcium and hydrogen ion concentration changes in slightly supersaturated solutions of pH 8.4 to 8.8 to which calcite seeds were added. Nancollas and Reddy found that the crystallization data satisfactorily fit a rate equation showing a first order dependence on the bulk concentrations of calcium and carbonate. The rate equation for calcite growth,

$$Ca^{++} + CO_3^{=} \rightleftharpoons CaCO_3, \qquad (1)$$

was expressed as follows:

$$-d[Ca^{++}]/dt = K_g\,[CaCO_3(s)]\,([Ca^{++}]\,[CO_3^{=}] - K_{sp}/f_2^{\,2}) \qquad (2)$$

where K_g is the growth reaction rate constant, K_{sp} is the solubility product of calcium carbonate, and f_2 is the mean divalent activity coefficient for calcium and carbonate ions. This equation reflects their assumption of a surface controlled process in which diffusion plays a negligible role in the rate determining step of the crystal growth. To test the assumption, crystal growth trials were repeated at different stirring rates. If diffusion had been critical, a growth rate change would have resulted. The growth rates determined were, however, independent of the stirring rate, supporting the proposed interfacial growth mechanism. Nancollas and

Reddy studied crystallization at 10, 25, and 40°C. The temperature dependence of the growth rate fits the Arrhenius equation,

$$\ln K_g = \ln A - E(RT)^{-1} \quad (3)$$

where A is an empirical constant and E is the activation energy. The activation energy for crystal growth was determined to be 46.1 $\pm$ 4.2 kJ/mole. The activation energy expected for a diffusion controlled reaction, however, would be considerably smaller, approximately 16.7 kJ/mole. Therefore, an interfacially controlled mechanism for calcite growth was again indicated (16).

Wiechers, Sturrock, and Marais (17) studied the applicability of the Nancollas and Reddy calcite growth rate expression to a wide range of total calcium and carbonate concentrations. Using pH measurements to monitor solution changes they confirmed the first order dependence of growth rate on bulk calcium and carbonate concentrations. The growth rate was again found to be independent of the stirring rate, and an activation energy of 43.1 $\pm$ 3.8 kJ/mole was determined. In addition, the rate constant increased with a rise in the initial pH of the supersaturated solutions over a pH range of 8 to 10.

The calcite growth rate equation was also confirmed at 25°C by Smallwood (18), using conductivity and pH measurements to monitor solution changes. Smallwood also studied the effects of four additives on the growth rates of calcite and aragonite. Three of the four additives - chondroitin sulfate, agar, and sodium alginate - slowed the growth rates of both polymorphs, whereas the fourth - albumin - slowed only the growth rate of the aragonite crystals.

Davies and Nancollas (19) postulated a mechanism by which additives slow crystal growth after showing that potassium benzoate, potassium eosin, sodium dodecylsulfate, potassium naphthalene-w-sulfonate, and cetyltrimethylammonium nitrate

slowed silver chloride crystal growth. They proposed that hydrated silver and chloride ions adsorbed on seed crystals in a monolayer. If the silver and chloride ions dehydrate simultaneously at an active growth site, the crystal grows. However, the presence of an additive in the monolayer at an active growth site prevents dehydration at that site and thus slows the growth rate of the crystal.

An additive may affect the crystal shape as well as the growth rate. Reitemeier and Buehrer (20) showed that minute amounts of a sodium hexametaphosphate additive caused distortions in calcium carbonate crystals which spontaneously precipitated. The crystals formed in the presence of the additive were larger and usually lacked the typical polyhedral faces of rhombic calcite. Also, McCall and Tadros (21) showed that the addition of carboxylic acid and phosphonic acid derivatives to calcium sulfate and calcium sulfite precipitations resulted in larger more blocky particles.

COMPLEXATION - THEORY

Complexation is the process by which a metal atom or ion is combined with an electron donor, called the ligand. Transition metals are the most commonly complexed metals. In general they form highly stable complexes, since they have three or more electrons available for interaction, at least one of which is in a d orbital. [Electrons from d orbitals generally form stronger bonds than s or p orbital electrons, since the diffuse nature of d orbitals gives rise to more effective overlapping (22).] Alkaline earth metals may also form complexes. These complexes are generally less stable than the corresponding complexes with transition metals, since alkaline earth metals have no electrons in incomplete d orbitals (22).

The ligand is commonly an organic molecule containing at least one of the following nonmetallic electron pair donors: nitrogen, oxygen, or sulfur (23). If

the ligand attaches to the metal atom with more than one donor group to form a ring, the resulting complex is called a chelate. Chelates are important in biological systems, in the dyeing of fabrics, in water hardness determinations, and in titrations of metal ions (23-24).

The formation of a complex may be expressed as follows:

$$M + nL \rightarrow ML_n \qquad (4)$$

where M = metal and L = ligand. The stability constant, K, of the complex is therefore,

$$K = [ML_n]/\ [M]\ [L]^n. \qquad (5)$$

The stability constant is influenced by several factors, including the number and size of the rings formed, the basicity of the chelating molecule, and the nature of the donor and metal atoms.

COMPLEXATION - LITERATURE REVIEW

Calcium Complexes

Calcium complexes with a variety of ligands (23) including dicarboxylic acids (e.g., malonic, oxalic, succinic, and maleic acids), amino acids (e.g., alanine, aspartic acid, and glycine), hydroxy acids (e.g., citric, gluconic, and lactic acids), phosphates, and 0,0'-dihydroxyazo dyes.

The ability of calcium to complex with certain ligands is especially important in biological systems. A recent review (25) has discussed the existence and structure of calcium complexes with carbohydrates, proteins, and thymine monophosphate. Studies of the associated stability constants were not reported.

A variety of experimental techniques has been used to study calcium complexes. Williams and Atalla (26) used changes in the carbon-carbon and carbon-oxygen stretching regions of the Raman spectra to establish the existence of an ethylene glycol complex with calcium. Calcium-45 isotope exchange was used in another study (27) to show instantaneous establishment of equilibrium in the calcium-ethylenediaminetetraacetic acid (EDTA) system. The calcium-EDTA complex, being very stable (log K = 10.7 at 25°C), is often used in determining water hardness (28). Solubility data, kinetic measurements and emf. measurements were used by Olin (29) to determine the structure and the stability constant (log K = 0.642 ± 0.015 at 25°C) of the calcium monohydroxide complex. This complex exists at high pH (e.g., at pH 11.3 at 25°) only as $CaOH^+$, not as a polynuclear complex.

The most common experimental technique for studying complexes is the potentiometric titration. Murakami et al. (30) used this technique to establish the stability constants of 4-carboxy and 4-sulfocatechol calcium chelates at 30°C and at a constant ionic strength of 0.1N. Westervelt (6), however, found the potentiometric method not applicable to the study of the calcium-catechol-4-sulfonate complex at an ionic strength of 0.92N over a temperature range of 5 to 80°C and at pH values of 10 or higher. He used instead ultraviolet absorption measurements in determining that the 1:1 complex had a moderate stability constant, log K = 3.82 ± 0.04, over the entire temperature range.

Iminodiacetic Acid Complexes

Iminodiacetic acid, $HN(CH_2COOH)_2$, is a crystalline solid with a molecular weight of 133.11 and a melting point of 247.5°C. It is slightly soluble in water and insoluble in alcohol and ether (31). Iminodiacetic acid (IDA) complexes with copper, nickel, cobalt, zinc, and cadmium were studied by Chaberek and Martell (32). Their objective was to examine the basis of metal ion affinity for the sequestering agent nitrilotriacetic acid. Their approach involved varying the number and type of

acid groups. Therefore, Chaberek and Martell determined the stabilities of several metal chelates of iminodiacetic acid and iminodipropionic acid. For both ligands the relative stabilities varied similarly with the metal ion in the complex: Cu > Ni > Co, Zn > Cd. The stability of the copper, nickel, and cobalt complexes follows the order of the ionization potentials of the metals (22). Chelate stability also depends on the ionic radius of the metal as reflected in the order Zn > Cd (22). With all of the metals, the iminodiacetic acid complex was shown to be more stable than the corresponding iminodipropionic acid complex (32).

Schwarzenbach et al. (33) studied the structure and stability of iminodiacetic and methyliminodiacetic acid complexes with calcium, magnesium, and barium. They showed that iminodiacetic acid formed the moderately stable 1:1 complex with calcium shown in Fig. 3. Two of the bonds, those between calcium and the acid oxygens, in the complex are essentially electrostatic, whereas the other two, those with nitrogen and the water oxygen, are coordinate bonds. The logarithm of the stability constant of the calcium-iminodiacetic acid complex (Ca-IDA) was determined to be 3.41 at 20°C. The magnesium-iminodiacetic acid complex is slightly more stable than Ca-IDA (log K = 3.66), whereas the corresponding barium complex is slightly less stable (log K = 1.67) than Ca-IDA. The same relative stabilities exist for the methyliminodiacetic acid complexes, reflecting again the importance of the ionic radius of the metal ion to chelate stability (33).

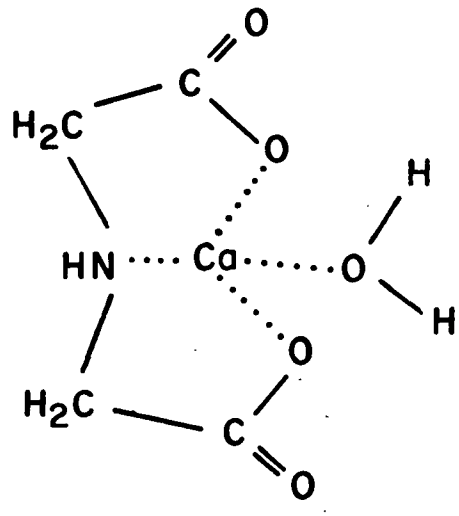


Figure 3. The Calcium - Iminodiacetic Acid Complex

EXPERIMENTAL APPROACH

Selection of a model system and a technique for studying crystal growth determined the experimental requirements of this study. The model system chosen contained the essential elements for studying calcite growth, a calcium source and a carbonate source. In addition, a complexing agent was added to simulate the effect of lignin degradation products in black liquor. The technique chosen for studying crystal growth involved monitoring solution changes as the growth of a large number of small crystals suspended in the solution proceeded. Proper selection of the initial solution conditions and the trial procedures eliminated or minimized all actions except crystal growth.

THE MODEL SYSTEM

To simulate black liquor, sodium carbonate and calcium nitrate were mixed with an organic complexing agent. Iminodiacetic acid (IDA) was chosen as the complexing agent since it forms a water soluble 1:1 calcium complex of known structure (33). Also, the stability constant of the Ca-IDA complex (log K = 3.47 at 25°C) is of the same magnitude as that of calcium complexes with lignin derivatives [i.e., for the calcium-catechol-4-sulfonate complex log K = 3.82 at 25°C (6)]. In the model system, pH adjustment to 10.0-10.8, with sodium hydroxide, ensured dissociation of the iminodiacetic acid. The pH was restricted throughout the study to a value below 11.3 to prevent formation of the calcium monohydroxide complex ($CaOH^+$) (29). Since only the calcite form of calcium carbonate is thermodynamically stable at room temperature and atmospheric pressure, (12) all seed crystals used were calcite.

THE TECHNIQUE

Five mechanisms are involved in scaling (1): 1) nucleation, 2) diffusion of the species to the crystallization surface, 3) deposition on surfaces, 4) removal by

shear stresses caused by flowing liquid, and 5) aging. The technique chosen for this study focused only on the deposition function. Adding seed crystals to a metastable supersaturated solution has been shown to result in crystal growth (16-18) without inducing nucleation. It has been further demonstrated (16-18) that calcite growth in a seeded metastable supersaturated solution is controlled by the incorporation of molecules into the crystal surface. Diffusion of the molecules to the surface was found to be insignificant in the growth rate expression (16-18), probably due to the slow, constant stirring. In this study, the stirring rate was also kept slow and constant to minimize shear stresses in the system. In addition, crystallization runs were limited to less than one hour, to reduce aging effects. Changes monitored in the supersaturated solution as growth occurred were thus interpreted as due solely to the deposition of calcium and carbonate ions into the crystal lattice.

In this study, changes in the solution composition were monitored by conductivity and pH. These measurements, used also by Smallwood (18), are nondestructive and accurate. However, interpretation of the experimental data requires knowledge of the equivalent conductance of a series of dilute solutions for the ions involved. Therefore, using the conductance of a series of dilute solutions of the ions and the data handling method of Shedlovsky (34), the equivalent conductance at infinite dilution was obtained for all ions present. Conductivity and pH data in crystallization runs could then be converted to ion concentrations.

The iminodiacetic acid dissociation constants and the calcium-iminodiacetic acid complex stability constants were determined at the temperatures under investigation, 25, 35, and 45°C, by potentiometric titration. The potentiometric method was selected, since it has been used in previous studies of iminodiacetic acid complexes (32,33) with calcium and other metals.

RESULTS AND DISCUSSION

The investigation of calcite growth in the presence of iminodiacetic acid required examination of the limiting equivalent conductance and a thorough characterization of the calcium - iminodiacetic acid complex. The results of the limiting equivalent conductance and complex characterization studies were then used to interpret conductivity and pH changes detected as calcite growth proceeded in the presence of the calcium complexing agent. A calcite growth mechanism is proposed and applied to the results of the growth studies and to the mechanism of scaling in black liquor evaporators.

LIMITING EQUIVALENT CONDUCTANCE

Interpretation of the conductivity measurement used to follow crystal growth (as outlined on page 46) requires knowledge of the limiting equivalent conductance of ions present in the growth solution. Therefore, the limiting equivalent conductances at infinite dilution, Λ_o, for sodium nitrate, sodium hydroxide, potassium bicarbonate, sodium carbonate, and sodium iminodiacetate were determined at 25, 35, and 45°C. For each salt, the conductivity, κ, of several dilute solutions was measured. The equivalent conductance, Λ, ($\Lambda = \kappa/c$; c = solute concentration) was then extrapolated to the hypothetical state of infinite dilution (c = o) using the Shedlovsky method (34). The limiting equivalent conductance at infinite dilution for the anion alone, Λ^o_-, was calculated by subtracting the corresponding value for the cation, Λ^o_+ [known from the literature (36)], from the limiting equivalent conductance of the salt, Λ_o.

$$\Lambda_o - \lambda^o_+ = \lambda^o_- \qquad (6)$$

(See Appendix I for a more complete discussion of the conductivity theory.)

The limiting equivalent conductances determined for the anions in this study are summarized in Table I. Table I also includes, in parentheses, previously reported values (36) for the anions studied and for the cations in the growth system, sodium and calcium. The limiting equivalent conductances, λ_o, determined at 25°C in this study agree satisfactorily with the values reported in the literature at 25°C. [The literature values reflect a summary of equivalent conductance studies (36) conducted prior to 1959 with equipment of more limited accuracy than is currently available.]

TABLE I

LIMITING EQUIVALENT CONDUCTANCE

	Limiting Equivalent Conductance, λ_o, cm^2/ohm-equivalent		
Ion	25°C	35°C	45°C
Na^+	(50.10)	(61.5)	(73.7)
Ca^{++}	(59.50)	(73.2)	(88.2)
NO_3^-	75.04 (71.46)	(85.48)	98.92
OH^-	197.2 (198.3)	206.2	216.6
HCO_3^-	49.83 (44.5)	53.68	63.26
$CO_3^=$	60.75 (69.3)	85.68	102.37
$IDA^=$	20.65	25.16	33.36

() indicates a value from reference (36).

From Table I it is observed that λ_o for each ion increases as the temperature was raised from 25°C to 45°C.

COMPLEX CHARACTERIZATION

Iminodiacetic acid dissociates in two steps. The first dissociation step,

$$H_2IDA \rightarrow H^+ + HIDA^-, \qquad (7)$$

leads to a dissociation constant, k_1, which may be expressed as:

$$k_1 = (H^+)\ (HIDA^-)/(H_2IDA). \tag{8}$$

Preliminary determinations indicated that k_1 has no effect in the characterization of the calcium-iminodiacetic acid complex. Therefore, only the second iminodiacetic acid dissociation constant influences the complex stability constant. In this study, potentiometric titrations were used to determine these constants at 25, 35, and 45°C. Further characterization of the calcium-iminodiacetic acid complex involved examining the dissociation rate of the complex.

The second dissociation step of iminodiacetic acid,

$$HIDA^- \rightarrow H^+ + IDA^=, \tag{9}$$

leads to a dissociation constant, k_2, which is expressed as follows:

$$k_2 = (H^+)\ (IDA^=)/(HIDA^-). \tag{10}$$

As shown in Table II, k_2 is temperature dependent. It increases from 1.66×10^{-10} at 25°C to 4.17×10^{-10} at 45°C.

The formation of the calcium-iminodiacetic acid (Ca-IDA) complex,

$$Ca^{++} + IDA^= \rightarrow Ca\text{-}IDA, \tag{11}$$

is characterized by the stability constant, K, which may be expressed as:

$$K = (Ca\text{-}IDA)/((Ca^{++})(IDA^=)). \tag{12}$$

Table II shows that K is also temperature dependent. K decreased with temperature from 2951 at 25°C to 1718 at 45°C.

TABLE II

IMINODIACETIC ACID

Acid Dissociation and Calcium Complex Stability Constants

Temperature, °C	Second Acid Dissociation, k_2	Calcium Complex Stability, K
25	1.66×10^{-10}	2951
35	3.23×10^{-10}	2399
45	4.17×10^{-10}	1718

In the calcite growth system, the dissociation rate of the Ca-IDA complex could influence the availability of ionic calcium. Therefore, the calcium-iminodiacetic acid complex equilibrium was displaced by the addition of a strong calcium complexing agent, ethylenediaminetetraacetic acid (EDTA) as shown in Eq. (13).

$$\begin{array}{c} \text{Ca-IDA} \rightleftharpoons \text{Ca}^{++} + \text{IDA}^{=} \\ + \\ \text{EDTA} \\ \downarrow \\ \text{Ca-EDTA} \end{array} \qquad (13)$$

The rate at which the Ca-IDA complex dissociated to reestablish equilibrium was monitored with conductivity measurements. At each temperature under investigation, the conductivity decreased within 15 seconds after the EDTA was added and then remained essentially constant (see Table III and Fig. 4). The initial drop in conductivity, e.g., from 2.41 to 2.29, indicated that EDTA complexed with the ionic calcium. Also during the initial conductivity drop, a portion of the Ca-IDA complex dissociated to reestablish the complex equilibrium. The equilibrium is reflected in the constancy of the subsequent conductivity measurements. The Ca-IDA complex thus serves as a calcium source in the calcite growth system, dissociating instantaneously to release ionic calcium for crystal growth.

TABLE III

CHANGE OF RELATIVE CONDUCTIVITY AS A FUNCTION OF TIME AFTER ADDITION OF EDTA TO A Ca-IDA COMPLEX

Time, seconds	Relative Conductivity
0	2.41
15	2.29
30	2.28
1170	2.28
1250	2.27
1570	2.27
2070	2.26

Conditions: $IDA_T/Ca_T = 1.881$; $Ca_T/EDTA_T = 59.326$; at 45°C

THE STUDY OF CALCITE GROWTH

After investigating limiting equivalence and characterizing the complex, calcite growth was monitored in the presence of the iminodiacetic acid complexing agent. Reaction solutions were prepared containing the iminodiacetic acid and equal concentrations of calcium and carbonate (0.0005M). The conductivity and pH changes in the solutions resulting from the addition of calcite seed crystals were then monitored.

Growth Solution Conductivity

Various IDA concentrations were investigated in this study. A decrease in conductivity after addition of the seed crystals was observed by Smallwood (17) in his studies of calcium carbonate crystal growth. He interpreted the conductivity decrease as the transfer of ionic calcium and carbonate from the solution phase to the solid crystals or, in other words, crystal growth. As shown in Table IV,

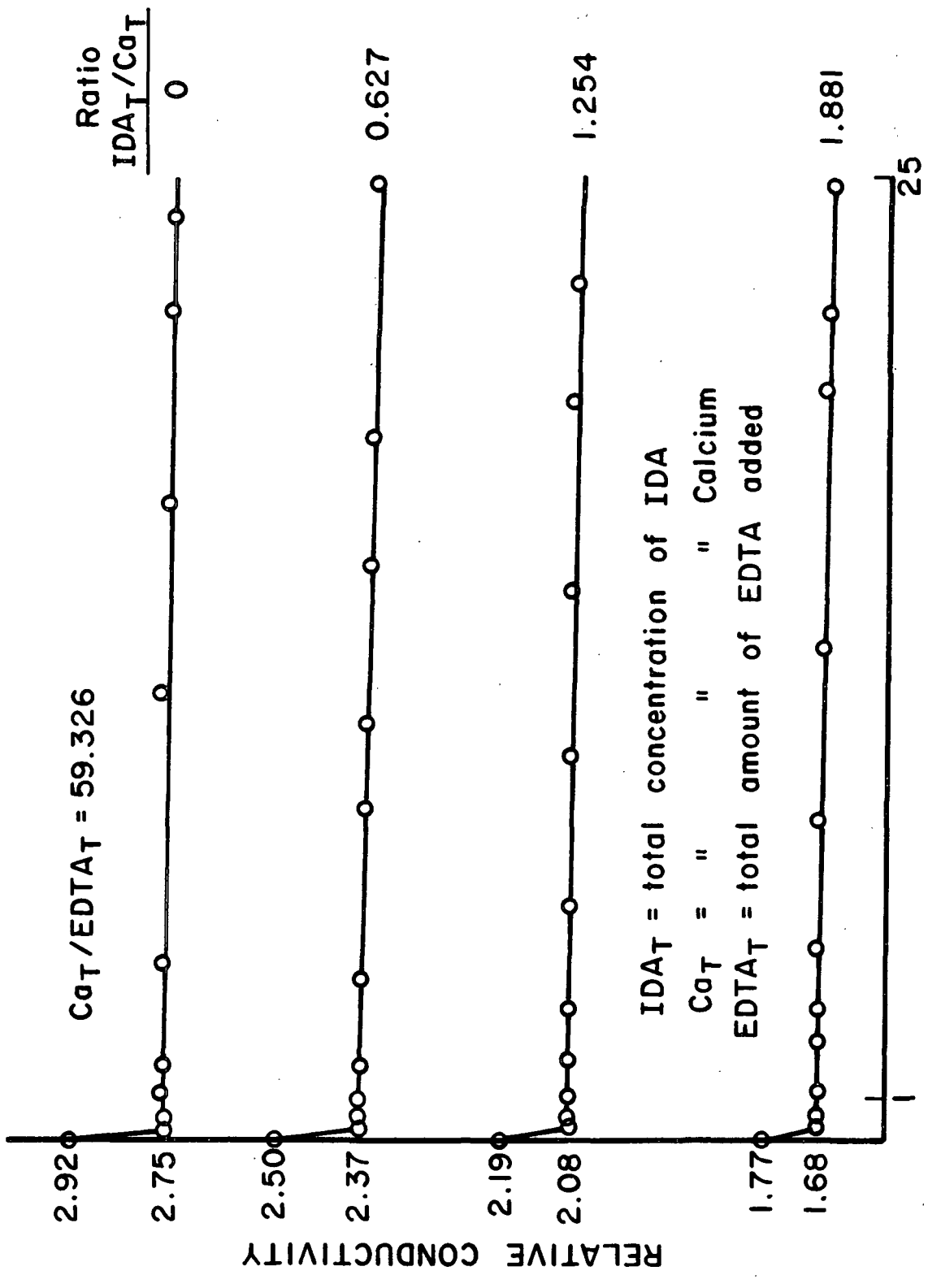


Figure 4. Changes of Relative Conductivity During Dissociation of the Ca-IDA Complex after the Addition of EDTA

crystal growth occurs when the iminodiacetic acid to calcium ratio in the system is low, 3.33 at 25°C and 6.25 at 45°C. Increasing the concentration of IDA to ratios of 6.25 and 6.67 at 25°C and 45°C, respectively, causes the solution conductivity to remain essentially constant after the seed crystals are added. The essentially constant conductivity reflects the constancy of ionic concentrations present in saturated solutions. When the IDA concentration is increased to 8.0 moles IDA/mole of calcium at 45°C, an increase in conductivity occurs after addition of the seed crystals. This indicates an increase in ionic calcium and carbonate concentrations caused by dissolution of the seed crystals. Further increases in the IDA concentration at 25°C and 45°C also cause dissolution of the seed crystals.

TABLE IV

CALCITE GROWTH IN THE PRESENCE OF IMINODIACETIC ACID, pH 10.0

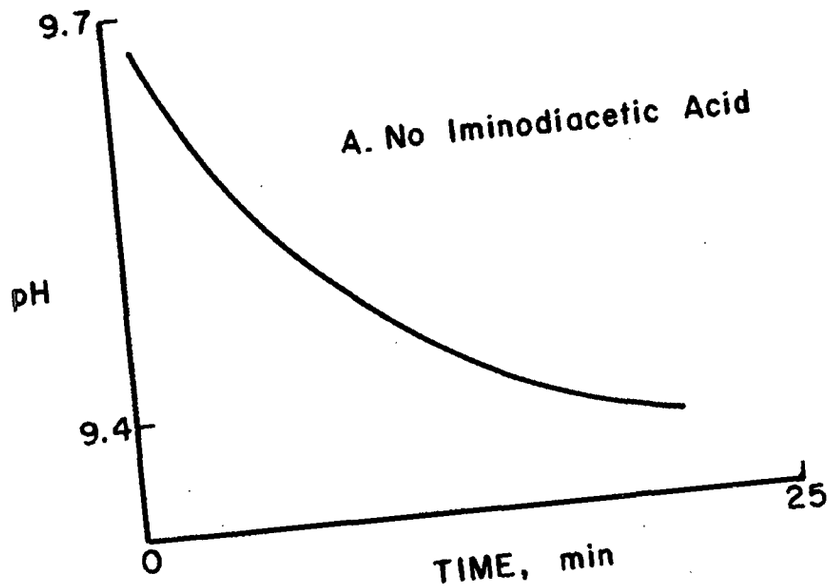
Temperature, °C	Total IDA/Total Calcium				
	3.33	6.25	6.67	7.14	8.0
25	G	S	S	S	S
45	G	G	S	S	D

G-growth, S-saturation, D-dissolution.

The ratio of 3.33 moles IDA/mole of calcium was used in all subsequent calcite growth trials to ensure growth at all temperatures investigated in the presence of a substantial quantity of iminodiacetic acid.

Growth Solution Alkalinity

Calcite growth in a supersaturated system without IDA results in a decrease in pH, as can be seen in Fig. 5A. The removal of carbonate ions from the liquid phase causes a portion of the bicarbonate ions present to dissociate, reestablishing the



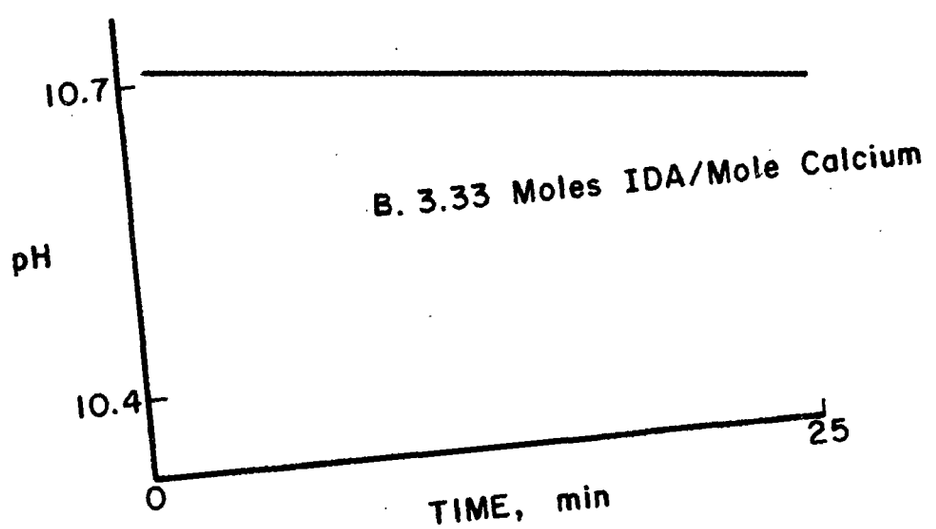


Figure 5. The Influence of IDA on the pH During Crystal Growth

carbonate-bicarbonate equilibrium. Some of the hydroxide originally present is thus neutralized.

$$OH^- + HCO_3^- \rightleftharpoons H^+ + CO_3^= + OH^- \rightarrow H_2O + CO_3^= \quad (14)$$

The presence of iminodiacetic acid buffers the calcite growth system (see Fig. 5B). The dissociation of the Ca-IDA complex as growth proceeds and the subsequent reestablishment of the iminodiacetic equilibrium increases the hydroxide content of the solution.

$$Ca\text{-}IDA + H_2O \rightarrow Ca^{++} + IDA^= + H_2O \rightleftharpoons Ca^{++} + HIDA^- + OH^- \quad (15)$$

The buffering effect of iminodiacetic acid was observed at each of the temperatures investigated: 25, 35, and 45°C.

The alkalinity level of two growth solutions prepared with equal chemical concentrations depends on the solution temperature. As can be seen in Table V, the pH of identically prepared solutions is 11.24 at 25°C and 10.79 at 45°C. At 45°C the lower pH shifts the iminodiacetate equilibrium toward $HIDA^-$,

$$IDA^= + H \rightarrow HIDA^-, \quad (16)$$

resulting in less $IDA^=$ available for complexation with calcium. Coupled with the lower stability of the Ca-IDA complex at 45°C, this results in less complex being formed. Therefore, more calcium will be present in the ionic form. The ionic calcium content of the 25°C solution in Table V is 8.64×10^{-5}M, whereas in the 45°C solution the ionic calcium concentration (1.164×10^{-4}M) is 35% greater.

The effect of temperature on the concentration of ionic calcium was also reported by Westervelt (6). Westervelt studied the temperature dependence of the stability of the calcium-catechol-4-sulfonate complex, Ca-C4S, from 5°C to 80°C.

His results indicated that a decrease in pH resulted when the temperature was raised. The pH decrease caused a shift of the catechol ligand from its totally dissociated form to the partially dissociated form. Only the totally dissociated form of the catechol ligand can complex with calcium, so the shift leads to an increase in the concentration of ionic calcium.

TABLE V

EFFECT OF HEATING, EQUIVALENT INITIAL CONCENTRATIONS

Solution Variable	25°C	45°C
Total calcium, M	0.00025	0.00025
Total IDA, M	0.0008325	0.0008325
IDA/Ca	3.33	3.33
mL 1.0M NaOH	1.5	1.5
pH	11.24	10.79
$HIDA^-$, M	0.000028	0.0000312
Total $IDA^=$, M	0.0008046	0.0008301
Ca-IDA, M	0.0001636	0.0001336
Ionic calcium	0.0000864	0.0001164

The concentration of the Ca-IDA complex formed in a growth solution can be controlled by adjusting the pH of the solution. The composition of two pH 10 solutions containing 1.60 moles of iminodiacetic acid and one mole of calcium, one at 25°C and the other at 45°C, is shown in Table VI. The pH adjustment with sodium hydroxide to 10.0 at each temperature causes almost 50% of the partially dissociated acid, $HIDA^-$, present at 25°C to become fully dissociated at 45°C. Although this represents a 29% increase in the amount of the fully dissociated, complexing form of the acid, $IDA^=$, the concentration of complex is essentially unchanged. The lower stability of the complex at 45°C causes the complex concentration in the 45°C solution to be only 2% higher than at 25°C. Therefore, in calcite growth systems

prepared with equal total chemical concentrations and adjusted to the same pH level at each temperature, the complex concentration will be essentially constant in the temperature range of this study. If the pH is not adjusted to the same level at each temperature however, substantially less complex will be formed at 45°C, leading to a larger concentration of ionic calcium. Therefore the availability of ionic calcium in calcite growth solutions depends on both temperature and the pH.

TABLE VI

EFFECT OF HEATING ON COMPOSITION, pH = 10.0

Temperature, °C	IDA moles	Calcium moles	$HIDA^-$ moles	$IDA^=$ moles	Ca-IDA moles
25	1.60	1.00	0.60	1.00	0.98
45	1.60	1.00	0.31	1.29	1.00

Crystal Analysis

In addition to monitoring solution changes, the seed crystals used in growth trials were examined for organic content and crystal form. Fresh seed crystals and samples of crystals from growth trials at each temperature under investigation were analyzed by infrared spectroscopy, the Kjeldahl nitrogen test, and by x-ray diffraction. The presence of iminodiacetic acid in the growth solution did not cause detectable changes in the seed crystals.

Growth Rate

The growth rate of calcite crystals in a supersaturated solution has been described in the literature (16-18) by the following expression:

$$-d(Ca^{++})/dt = K_g\ [CaCO_3(s)]\ ([Ca^{++}]\ [CO_3^{=}]\ -K_{sp}/f_2^2). \qquad (17)$$

Using the computer programs presented in Appendix VII, conductivity and pH data collected in growth solutions containing IDA are combined with known equilibrium

constants to calculate ionic calcium and carbonate concentrations in the growth solution at time intervals during a growth run. The growth rate constant is then proportional to the slope of $-d(Ca^{++})/dt$ vs. $(Ca^{++})\ (CO_3^{=})-K_{sp}/f_2^2$.

The growth rate constants calculated for growth solutions containing 3.33 moles IDA per mole of calcium were substantially lower than those predicted by calcite growth studies (16-18) containing no additives. At 25°C, a growth rate constant of 4.0 mol^{-1} L min^{-1} (mg seeds/100 mL suspension)$^{-1}$ has been determined (18). Extrapolation of growth rate constants determined from 10°C to 40°C (16-17) in solutions containing no IDA predicted growth rate constants of 6.49 and 8.81 mol^{-1} L min^{-1} (mg seeds/100 mL suspension)$^{-1}$ at 35°C and at 45°C, respectively. As can be seen in Table VII, however, the growth rate constants determined with 3.33 moles IDA/mole of calcium present in the growth solution are 3.43, 4.28, and 3.78 mol^{-1} L min^{-1} (mg seeds/100 mL suspension)$^{-1}$ at 25, 35, and 45°C. A mechanism proposed by Davies and Jones (14) can be applied to explain how the presence of iminodiacetic acid lowers the growth rate constant.

TABLE VII

GROWTH RATE CONSTANTS

	Growth Rate Constants		
IDA/Calcium	25°C	35°C	45°C
0.00	4.0	6.49	8.81
3.33	3.43	4.28	3.78

CALCITE GROWTH MECHANISM

Davies and Jones (14), in a study of silver chloride growth, proposed that a monolayer of hydrated ions on crystals in aqueous solution was involved in the mechanism for a surface controlled crystal growth reaction. As applied to calcium carbonate growth, their mechanism states that, in an unsaturated solution, hydrated

calcium and carbonate ions leave the monolayer faster than they are replaced from the solution. Hydration of the calcium carbonate ions on the crystal surface then occurs to fill the monolayer. This dissolution continues until the solution becomes saturated. In a saturated solution, ions enter the adsorbed monolayer at the same rate as ions leave.

In a supersaturated solution, ions reach the surface faster than ions are leaving. Most of the ions will collide with and rebound from the surface of the monolayer as shown in Fig. 6. If, however, a calcium and carbonate ion arrive simultaneously at a growth site, they can enter the monolayer by causing the underlying pair to become dehydrated (see Fig. 7). The simultaneous dehydration of calcium and carbonate ions at a growth site constitutes crystal growth.

Davies and Jones (14) did not specify the mechanism by which the underlying ion pair dehydrates. The impact of collision when the hydrated calcium and carbonate ions arrive at the hydrated monolayer may be sufficient to force the waters of hydration into the liquid phase.

The mechanism proposed by Davies and Jones (14) was expanded by Davies and Nancollas (19) to explain the growth-inhibiting action of additives. The applicability of the mechanism to calcium carbonate crystal growth studies in the presence of additives was first suggested by Smallwood (18). In this study the mechanism was applied to the calcite growth system containing iminodiacetic acid. Fully and partially dissociated iminodiacetic acid ions ($IDA^{=}$ and $HIDA^{-}$) will therefore be present in the adsorbed monolayer with the calcium and carbonate ions. However, the iminodiacetate ions do not enter the crystal lattice. (This is evident from the lack of nitrogen in seed crystals analyzed after growth trials.) Instead, the iminodiacetate ions may block active growth sites as shown in Fig. 8. Restating, if calcium and carbonate ions arrive simultaneously at a point where the monolayer

contains an iminodiacetic acid species, a collision will occur. However, dehydration and incorporation of the underlying pair will not proceed. Therefore, crystal growth is restricted to those collisions occurring where the monolayer contains a calcium carbonate ion pair at a growth site.

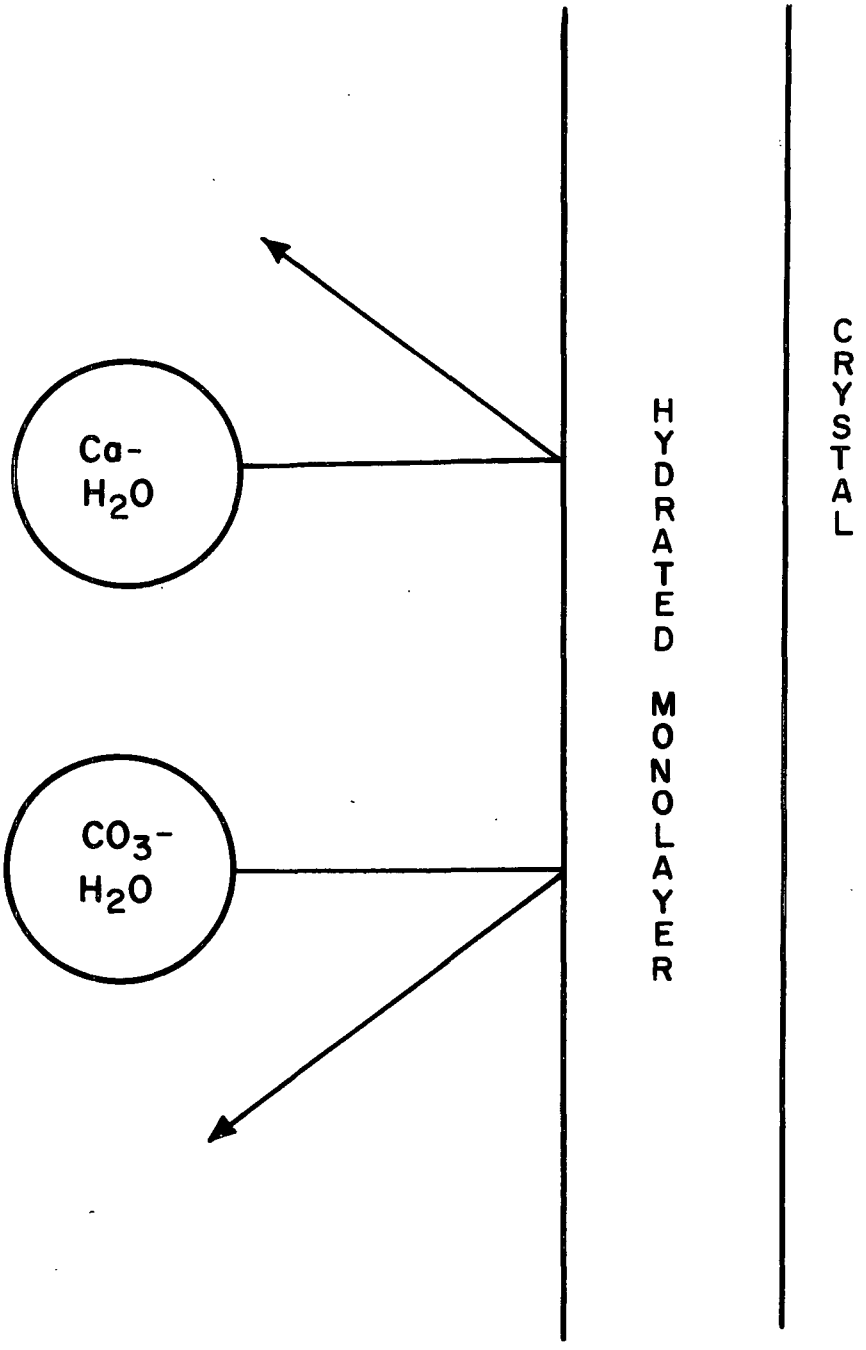


Figure 6. Elastic Collisions of Hydrated Ions with the Hydrated Monolayer

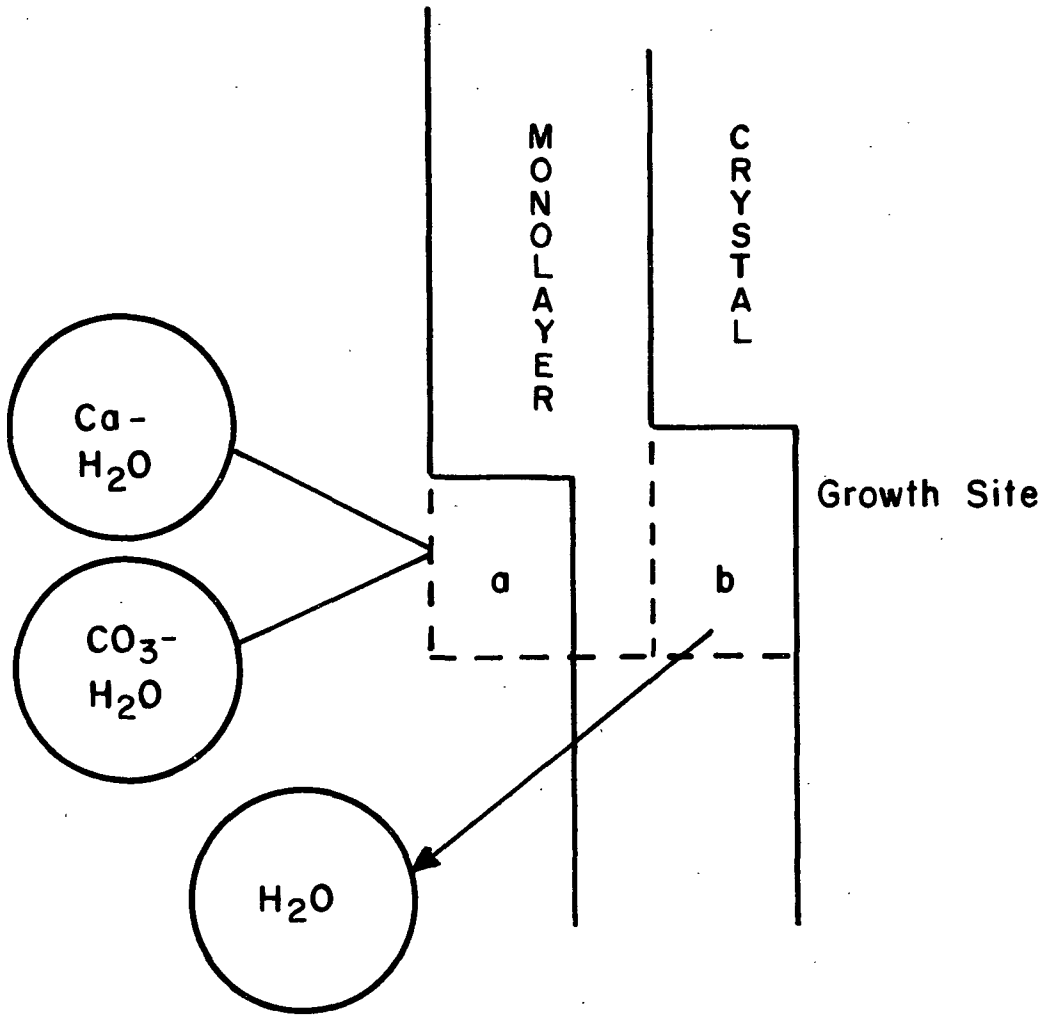


Figure 7. Crystal Growth by Dehydration of Ions at a Growth Site

As the temperature rises from 25°C to 45°C, the increased kinetic motion of the ions increases the possibility of simultaneous arrival of calcium and carbonate ions. Therefore, in the system without IDA, the growth rate constant increases with temperature, as was shown in Table VII where the constant is 4.0 at 25°C and 8.81 at 45°C. However, when IDA is present, although more calcium and carbonate ions arrive at the monolayer surface, the incorporation of those ions into the lattice is not increased. From Table I, where limiting equivalent conductances are listed, the

relative mobility of anions in the growth system can be inferred, since ionic mobility, u, is proportional to the ionic equivalent conductance, λ (35).

$$u(\text{cm sec}^{-1}\ \text{dyn}^{-1}) = N\lambda/(|z|F^2) = 6.469 \times 10^6\ \lambda/|z|\ (\text{cm}^2\ \Omega^{-1}\ \text{equiv.}^{-1}). \quad (18)$$

Iminodiacetate is, at all temperatures, less mobile than the other anions (bicarbonate, carbonate, and hydroxide) which may be in the adsorbed monolayer. Therefore, iminodiacetate ions which enter the monolayer are less likely to leave than other anions. This leads to the buildup of iminodiacetate ions depicted in Fig. 9, further blockage of active growth sites, and a lower growth rate constant.

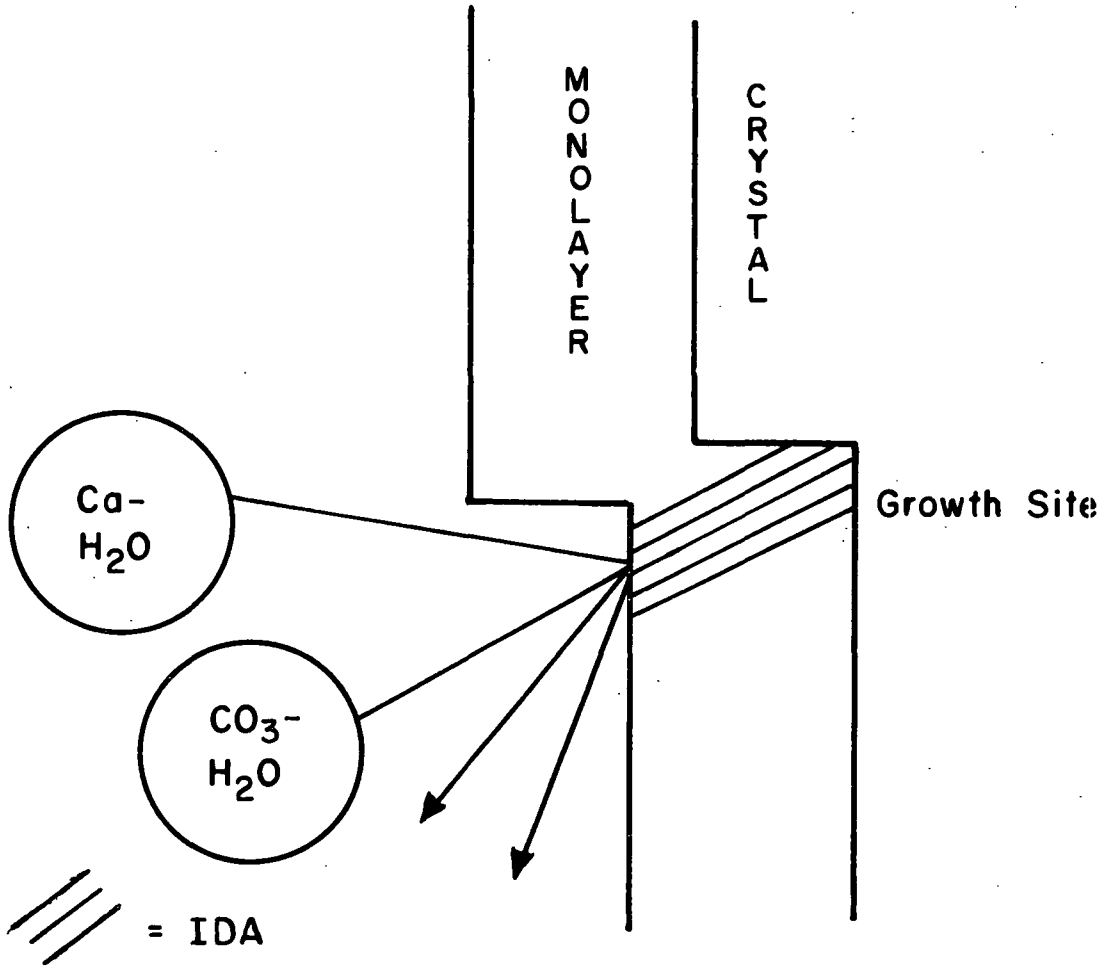


Figure 8. The Blocking of a Growth Site by IDA

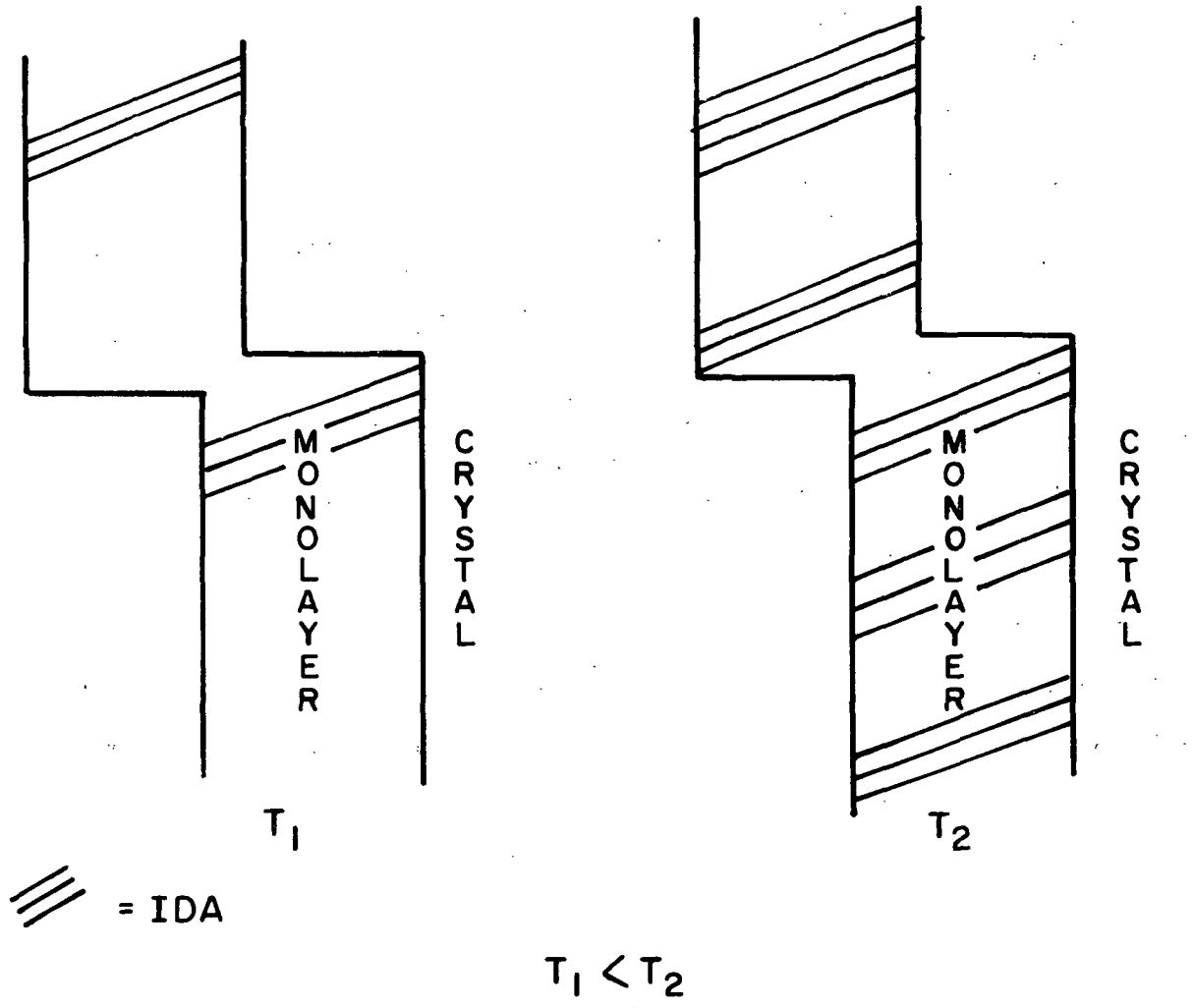


Figure 9. The Increase in Concentration of IDA in the Monolayer with Increasing Temperature

Further indication of the monolayer on crystal surfaces arises from the lack of predictability of the saturation condition based on solution properties. To illustrate, since all growth solutions contain 2.5×10^{-4}M total carbonate and bicarbonate, setting the pH at 10.0 will dictate the carbonate-bicarbonate ratio (from the bicarbonate-carbonate equilibrium constant). Then, knowing the carbonate content and the solubility product of calcium carbonate, the concentration of ionic calcium in a saturated solution can be calculated,

$$K_{sp}/(CO_3^{=}) = (Ca^{++}). \quad (19)$$

Since the total calcium content of all growth solutions was 2.5×10^{-4}M, the amount of calcium tied up in the Ca-IDA complex could be calculated by difference. Knowing the complex stability constant, the IDA dissociation constant, and the pH, the amount of total IDA in the saturated system could be calculated. Expressed as a ratio of total IDA to total calcium, the calculations predict saturation at 25°C for a ratio of 8.33 and at 45°C for a ratio of 25.0. Experimentally, however, saturation, as noted in Table IV, occurred at ratios of 6.25 at 25°C and 6.67 at 45°C (see Table VIII). The difference between the experimental determinations and the predicted values is caused by the blocking action of the iminodiacetic acid ions in the surface monolayer. The predicted ratio reflects only the reduction in calcium ion availability resulting from complexation. In real growth solutions, however, a smaller quantity of IDA results in saturation, since the acid species block growth sites as well as limit ionic calcium.

TABLE VIII

SATURATION RATIOS, IDA/Ca, pH 10.0

Temperature, °C	Predicted Ratio	Experimental Ratio
25	8.33	6.25
45	25.0	6.67

The results of this study indicate that two mechanisms are involved as the presence of the complexing agent lowers the growth rate of calcite. First, the complexing agent ties up ionic calcium in the complex, reducing the level of supersaturation. Second, active growth sites on the seed crystals are blocked by the presence of iminodiacetate species in the adsorbed monolayer of hydrated ions which surrounds the crystals. Combined with Westervelt's results (6) showing that the

calcium distribution in a complex system is a function of temperature, base concentration, and ionic strength, the results of this study expand upon the proposed scaling mechanism of Grace and Frederick (4).

Grace and Frederick proposed that the calcium complexes formed in black liquor dissociated at high temperatures, releasing ionic calcium for crystal growth. Therefore, temperature and chelate stability are the key variables in their proposed mechanism. Westervelt (6) determined that, in the 5 to 80°C temperature range, base concentration and ionic strength also determine the ionic calcium concentration present in a model black liquor. In this study the level of basicity controlled the ionic calcium concentration of solutions at 25°C to 45°C by shifting the equilibrium between the complexing form, $IDA^{=}$, and the partially dissociated form, $HIDA^{-}$, of the iminodiacetic acid. In addition, the blocking of crystal growth sites by the complexing agent was indicated. This latter action was not considered by Grace and Frederick (4).

To summarize, this study suggests that the mechanism of scaling in black liquor evaporators may be much more complex than previously thought. Temperature, chelate stability, basicity, ionic strength, and the blocking action of additives in a crystal growth system may all be important considerations in the mechanism of scaling.

CONCLUSIONS

The present study has expanded knowledge of the temperature dependence of ionic limiting equivalent conductances and the stability constant of iminodiacetic acid (IDA).

In addition, the relationship between temperature, pH, and ionic calcium available for calcite growth was also studied. In growth solutions at 25°C and 45°C, prepared with equal chemical concentrations, the lower pH and the lower stability constant of the calcium-iminodiacetic acid complex at 45°C led to an increased availability of ionic calcium in the 45°C solution.

The study of the effect of iminodiacetic acid on the growth rate of calcite indicated that moderate additions of IDA (3.33 moles IDA/mole of calcium) reduced the growth rate constant of calcite at all temperatures investigated. Concentrations of IDA in excess of 6.67 moles IDA/mole of calcium inhibited growth completely.

The concentration of IDA needed for growth inhibition is not predicted solely by the complexation process. A mechanism previously proposed by Davies and Jones has been applied to calcite growth to explain the additional role of IDA molecules in the calcite growth reaction. In the mechanism, a monolayer of hydrated ions surrounds each seed crystal. Calcium and carbonate ions colliding with the monolayer at an active growth site may enter the monolayer by causing dehydration of the underlying ions. The entry of the dehydrated ions into the crystal lattice constitutes crystal growth. However, the presence of ions of iminodiacetic acid in the monolayer blocks active growth sites, since the iminodiacetic acid cannot enter the crystal lattice. It is the blocking action of the iminodiacetate ions which increases the effectiveness with which IDA inhibits calcite crystal growth. Based

on the proposed mechanism, it is suggested that scaling is not only a function of available calcium, but also depends on the blocking action of lignin fragments in the black liquor.

SUGGESTIONS FOR FUTURE WORK

The severity of evaporator scaling at temperatures above 120-130°C noted by Grace and Frederick (4) is not addressed in this study. Extension of the temperature range could be informative and may indicate some effect not noted at lower temperatures.

In addition, the indication in this study that large quantities of complexing agent can inhibit calcium carbonate crystal growth warrants further study. An investigation of pulping conditions which might convert large quantities of lignin to fragments which can complex with calcium is suggested.

The mechanism proposed in this study has yet to be proven. An investigation of the blocking action of a wide variety of growth solution additives may illuminate the chemical or physical nature of the adsorption of the additives.

EXPERIMENTAL

CHEMICALS

All of the chemicals used in this study were reagent grade. Only two chemicals, iminodiacetic acid and calcium carbonate seed crystals, were not used in the purchased form. The iminodiacetic acid was purified by recrystallization, and calcium carbonate seed crystals were precipitated to ensure purity and to minimize agglomeration of the particles.

The 99% pure iminodiacetic acid supplied by Eastman Chemicals was dissolved in hot triply distilled water. The solution was then filtered hot through Whatman 42 ashless filter paper. The iminodiacetic acid, which recrystallized as the solution cooled, was dried at 100°C and stored over calcium chloride.

Calcium carbonate seed crystals for growth trials were prepared by dropwise addition of 0.2M sodium carbonate (Na_2CO_3) to 0.2M calcium nitrate ($Ca(NO_3)_2$) at 25°C with constant stirring. Sodium and nitrate ions were removed by pressurized ultrafiltration in an Amicon stirred cell. Triply distilled water was added to replace sodium nitrate solution removed. The seed crystals were then freeze-dried and stored over calcium chloride to prevent agglomeration.

WATER

All solutions were prepared with freshly boiled, triply distilled (3D) water. Deionized, distilled water (1D) from a commercial still was redistilled from a solution of 0.02% $KMnO_4$ and 0.05% KOH (w/w) to remove any organic impurities. The third distillation was from a pot containing no additives. The conductivity of the 3D water was checked regularly to ensure purity.

GLASSWARE

All of the glassware used in solution preparations was thoroughly cleaned prior to use. The first wash, with Alconox, degreased the pyrex glassware. The glassware was then soaked in concentrated nitric acid, followed by concentrated sodium hydroxide. Washing with dilute nitric acid followed, and subsequently the glassware was washed with dilute sodium hydroxide. Thorough rinsing with 1D and 3D water followed. After each use, the glassware was cleaned with dilute hydrochloric acid to dissolve calcium carbonate and thoroughly rinsed with 1D and 3D water.

PROCEDURES AND TECHNIQUES

The experimental procedures used in this study fell into three categories: equivalent conductance determinations, complex characterization, and crystal growth studies.

Equivalent Conductance Determinations

The equivalent conductance at infinite dilution of sodium nitrate, sodium hydroxide, potassium bicarbonate, sodium carbonate, and sodium iminodiacetate was determined at 25, 35, and 45°C in a carbon dioxide-free atmosphere. For each chemical, a series of dilute solutions was prepared by volumetric dilution of a stock solution. (The stock solutions were prepared by dissolving a weighed quantity of chemical in freshly boiled 3D water.) The solutions were then equilibrated in a circulated water bath controlled to the temperature under investigation $\pm$ 0.01°C by a Model 1460 BKU Thermomix Controller manufactured by B. Braun. The conductivity of each solution was measured using a model 9-324-24 conductivity cell by Fisher attached to a Markson Model 4403 combination conductivity-pH meter.

A pH-dependent equilibrium exists between carbonate and bicarbonate ions in aqueous solutions.

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad (20)$$

Therefore, the pH function of the Markson meter, a Model 476022 Corning pH electrode, and a calomel reference electrode were used to establish the alkalinity of the sodium carbonate and potassium bicarbonate solutions. The relative amounts of carbonate and bicarbonate then followed from the carbonate-bicarbonate equilibrium constant (4). The contributions of ions not pertinent to each equivalent conductance determination could then be removed. For example, the contributions of hydroxide and bicarbonate were subtracted from the total conductivity of the carbonate solutions in the determination of the equivalent conductance of the carbonate ion.

Equivalent conductance is defined as the solution conductivity per unit concentration of solute.

$$\Lambda = \kappa/c \qquad (21)$$

The Onsager equation (35) predicts a linear correlation between equivalent conductance and the square root of the concentration (see Appendix I for a discussion of conductivity theory).

$$\Lambda = \Lambda_o - (A + B\,\Lambda_o)\sqrt{c} \qquad (22)$$

However, since several approximations were involved in the derivation, the strict validity of the Onsager equation is limited to the hypothetical state of infinite dilution. Therefore, the empirically determined Shedlovsky (9) extension of the Onsager equation has been used to extrapolate experimentally determined equivalent conductances to infinite dilution (c = o).

$$\Lambda_o{}^1 = (\Lambda + A\sqrt{c})/(1 - B\sqrt{c}) = \Lambda_o + dc \qquad (23)$$

Complex Characterization

The stability constant of the calcium-iminodiacetic acid (Ca-IDA) complex was determined at the temperatures under investigation (25, 35, and 45°C). In the calculation of the stability constants, the iminodiacetic acid dissociation constants at each temperature were required. Therefore, both the iminodiacetic acid and the Ca-IDA complex were titrated with 0.1N sodium hydroxide. The pH determinations after each addition of base were converted by the direct algebraic method of Chaberek and Martell (32) to the dissociation constants of the acid and the stability constants of the complex.

In the low pH buffer region of the titration curve of the acid, the total concentration of iminodiacetic acid species, C_A, is

$$C_A = (H_2IDA) + (HIDA^-) \tag{24}$$

and

$$aC_A + (H^+) = (HIDA^-) \tag{25}$$

where a is the number of moles of base added per mole of amino acid present. Therefore, the first dissociation constant, k_1, which is defined as

$$k_1 = (H^+)\ (HIDA^-)/(H_2IDA), \tag{26}$$

can be expressed as

$$k_1 = (H^+)\ (aC_A + (H^+))/(C_A - (aC_A + (H^+))). \tag{27}$$

In the high pH buffer region, the concentration of H_2IDA may be neglected, so

$$C_A = (HIDA^-) + (IDA^{-2}) \tag{28}$$

and

$$(a - 1)C_A - (OH^-) = (IDA^{-2}). \tag{29}$$

where Λ_i is the equivalent conductivity of electrolyte i and C_i is the concentration of electrolyte i (g eq l^{-1}). The conductivity can be rewritten more explicitly as follows:

$$k_o = 2\Lambda_{CaCO_3}\ (CaCO_3) + 2\Lambda_{Ca(HCO_3)_2}\ (Ca(HCO_3)_2 + 2\Lambda_{Ca(OH)_2}\ (Ca(OH)_2) + \Lambda_{NaNO_3}\ (NaNO_3) + 2\Lambda_{Na_2IDA}\ (Na_2IDA) + \Lambda_{NaHIDA}\ (NaHIDA). \quad (40)$$

The equivalent conductance of each electrolyte is calculated using the Onsager equation (35) (see Appendix I):

$$\Lambda = \Lambda_o^- (A + B\Lambda_o)\ I^{1/2} \quad (41)$$

As a first approximation, the ionic strength is assumed to result solely from the sodium nitrate present. Using the measured conductivity and pH, the carbonate-bicarbonate equilibrium constant, the IDA dissociation constant, the Ca-IDA complex stability constant, and the ionic equivalent conductances at infinite dilution, the ionic calcium and carbonate concentrations can be calculated. A second approximation of the total ionic strength can be made based on the calculated concentrations of $CaCO_3$, $Ca(HCO_3)_2$, $Ca(OH)_2$, NaHIDA, and Na_2IDA. With a computer program (see Appendix VI), successive values of ionic calcium concentration are calculated until they agree within 1%.

Once the concentration of each species in the solution has been determined, the growth rate constant, K_g, can be calculated from the calcite growth rate expression (15-17)

$$-d\ (Ca^{+2})/dt = K_g\ (CaCO_3(s))\ ((Ca^{+2})(CO_3^{-2}) - K_{sp}/f_2^2). \quad (42)$$

The crystal growth studies also included examining the seed crystals for chemical and physical changes. The first analysis of calcium carbonate crystals for

adhering organic material involved a potassium bromide pellet in a Perkin Elmer Model 621 Grating Infrared Spectrophotometer. When no organic material was detected, the more sensitive Kjeldahl method was used to analyze for amino nitrogen groups. The TAPPI Standard T418 om-80 (Hengar modification) was used.

The seed crystals used in growth trials were analyzed by x-ray diffraction to determine any changes in the crystal form induced by growth in the presence of the complexing agent. A Norelco diffractometer with a nickel filtered copper K alpha radiation was used.

LIST OF SYMBOLS

A = electrophoretic constant = $82.4/(\varepsilon T)^{1/2}\eta$ for uni-univalent electrolytes

B = asymmetry constant = $8.20 \times 10^5/(\varepsilon T)^{3/2}$ for uni-univalent electrolytes

C_A = total acid concentration

C_M = total metal concentration

I = ionic strength = $1/2(c_i z_i^2)$

K = stability constant

K_g = growth rate constant

K_{sp} = solubility product

L = ligand

M = metal

T = absolute temperature

a = no. moles base added/mole of acid

b = Kohlrausch proportionality constant

c = concentration, moles/liter

d = Shedlovsky proportionality constant

f_2 = divalent activity coefficient

i = summation label

k_o = specific conductivity, Ω^{-1} cm^{-1}

k_1 = first dissociation constant

k_2 = second dissociation constant

o = infinite dilution

pH = $-\log (H^+)$

q = $|z_1 z_2| (\lambda^o_1 + \lambda^o_2)/[(|z_1| + |z_2|)(|z_2| \lambda^o_1 + |z_1| \lambda^o_2)]$

t = time

x = $(H^+)^2/k_1k_2 + (H^+)/k_2 + 1$

z = valence

Σ = summation

ε = dielectric constant of solvent

κ = conductivity

Λ = equivalent conductance of an electrolyte

Λ_o^1 = Shedlovsky constant of conductance

λ = equivalent conductance of an ion

η = viscosity of the solvent

1 = cation

2 = anion

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APPENDIX I

CONDUCTIVITY THEORY

Measurement of conductivity can be a useful analytical tool for monitoring solution compositions. Accuracy, reliability, and the nondestructive nature of such measurements enhance adaptability to corrosion studies, water quality control, and monitoring the growth of crystals from solution.

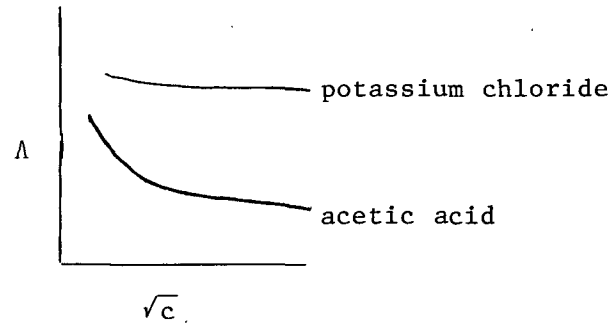
Conductivity measurements were first explained by Kohlrausch. He maintained that in an electric field, positive ions move in one direction while negative ions move in the other, producing a flow of charge in an electrically neutral solution. This concept, Kohlrausch's law of independent ionic migration, can be expressed mathematically:

$$\Lambda = \lambda_+ + \lambda_- \tag{43}$$

where Λ is the equivalent conductivity (the conductivity of an electrolyte solution containing one equivalent per given volume, i.e., $\Lambda = \kappa/c$), and λ_+ and λ_- are the equivalent conductivities of the ions involved (36). Electrically charged ions in real solutions influence each other, making Kohlrausch's law strictly valid only at the hypothetical state of infinite dilution (i.e., $c = 0$).

$$\Lambda_o = \lambda^o_+ + \lambda^o_- \tag{44}$$

Kohlrausch determined the equivalent conductivity, Λ_o, of strong electrolytes, by extrapolation of the linear dependence of experimentally determined values on the square root of the concentration. For weak electrolytes, i.e., those which do not dissociate completely in solution, the dependence is nonlinear.



Therefore, Kohlrausch combined Λ_o values for strong electrolytes to obtain Λ_o for a weak electrolyte.

EXAMPLE DETERMINATION OF Λ_o FOR ACETIC ACID

$$\Lambda_o, \text{ acetic acid (HAc)} = \lambda^o_{H^+} + \lambda^o_{AC^-}$$

$$\Lambda_{o,HAc} + \Lambda_{o,NaCl} = \lambda^o_{H^+} + \lambda^o_{Ac^-} + \lambda^o_{Na^+} + \lambda^o_{Ac^-}$$

$$= \lambda^o_{H^+} + \lambda^o_{Cl^-} + \lambda^o_{Na^+} + \lambda^o_{Ac^-}$$

$$= \Lambda_{o,HCl} + \Lambda_{o,NaAC}$$

$$\Lambda_{o,HAc} = \Lambda_{o,HCl} + \Lambda_{o,NaAC} - \Lambda_{o,NaCl}$$

Kohlrausch's experimentally determined relationship between the equivalent conductivity of strong electrolytes and concentration,

$$\Lambda = \Lambda_o - b\sqrt{c} \tag{45}$$

has been explained theoretically by Onsager and Fuoss (35). They proposed that the formation of ionic atmospheres caused ions to affect each other's motion. Two effects are involved. The first, the asymmetry effect, arises from the direct transfer of electric forces between the ions. The second, the electrophoresis effect, is a hydrodynamic effect.

The origin of the asymmetry effect is best described by Onsager and Fuoss (35): "When the ion starts moving, at first its atmosphere will be left behind; but the displaced ion will soon exert an electric pull on its lagging atmosphere, which will

continue to form around the ion as it moves along and to scatter in the rear." The motion of the ion will thus be slowed by an amount dependent on the dielectric constant and temperature of the solvent. [For uni-univalent ion pairs, this effect is $B\Lambda_o \sqrt{c}$, where $B = 8.20 \times 10^5/(\varepsilon T)^{3/2}$.]

The electrophoretic effect arises because "in the case of electrolytic conduction, a given ion does not move with respect to a medium at rest, but, since it is surrounded by an atmosphere of ions which move in the opposite direction, it actually travels with respect to a moving medium (35)." The magnitude of the effect depends on the dielectric constant, temperature, and viscosity of the solvent. [For uni-univalent electrolytes, the electrophoretic retardation effect can be expressed as $A \sqrt{c}$ where $A = 82.4/(\varepsilon T)^{1/2}\eta$.]

Combining the two retardation effects with Kohlrausch's experimental results led to the limiting form of the Onsager equation:

$$\Lambda = \Lambda_o - (A + B\Lambda_o) \sqrt{c} \tag{46}$$

For solutions not composed solely of uni-univalent electrolytes, a more general form of the Onsager equation was obtained.

$$\Lambda = \Lambda_o - \left[\frac{2.801 \times 10^6 \, | z_1 \, z_2 | \, q \, \Lambda_o}{(\varepsilon T)^{3/2} \, (1 + \sqrt{q})} + \frac{41.25 \, (| z_1 | + | z_2 |)}{\eta \, (\varepsilon T)^{1/2}} \right] I^{1/2} \tag{47}$$

where $q = | z_1 \, z_2 | \, (\lambda^o_1 + \lambda^o_2)/[(| z_1 | + | z_2 |) \, (| z_2 | \lambda^o_1 + | z_1 | \lambda^o_2]$,

$I = 1/2(c_1 z_1^2 + c_2 z_2^2)$,

z = valence, and

c = moles/liter.

The Onsager equation is useful in interpreting the measured conductivity of a solution of known composition. Providing the equivalent conductance at infinite dilution, Λ_o, is known, the contribution of each electrolyte in the solution can be

determined. However, since the Onsager equation is strictly valid only as a limiting expression, many empirical extensions of Onsager's equation have been proposed for extrapolating experimentally determined equivalent conductances to infinite dilution. The extension proposed and tested by Shedlovsky in 1932 is usually used for determining Λ_o if the solutions involved do not exceed 0.1N (34). Shedlovsky rearranged the Onsager equation to give:

$$\Lambda_o{}^1 = (\Lambda + A\sqrt{c})/(1 - B\sqrt{c}) = \Lambda_o + dc. \qquad (48)$$

The term $\Lambda_o{}^1$ was introduced for linear extrapolation to infinite dilution. Using this extension, experimentally determined equivalent conductances can be extrapolated to infinite dilution to give Λ_o. Using Λ_o values and the Onsager equation, conductivity measurements can be interpreted with respect to solution composition.

APPENDIX II

DATA FROM WHICH THE LIMITING EQUIVALENT CONDUCTANCE WAS CALCULATED

$NaNO_3$, 25°C

Concentration[a]	Conductivity[b]	Λ	Λ_o[1]
0.0945	10.3	108.995	136.948
0.10933	11.89	108.753	138.792
0.13667	14.90	109.022	143.161
0.14096	15.29	108.470	143.139
0.16400	18.27	111.402	149.371
0.1762	19.5	110.670	150.095
0.1890	20.6	108.995	149.797
0.191334	21.37	111.6895	153.068
0.21867	24.27	110.9892	155.482
0.2467	27.3	110.661	158.230
0.2835	31.2	110.053	161.434

Λ_o[1] vs. c intercept: 125.143
Slope: 134.87
Corr.: 0.9848
125.143 - 50.1 = 75.04

$NaNO_3$, 45°C

Concentration[a]	Conductivity[b]	Λ	Λ_o[1]
0.07048	10.412	147.734	183.793
0.10933	15.895	145.3855	190.792
0.13667	19.900	145.6062	196.915
0.14096	21.443	152.122	205.021
0.16400	23.780	145.00	201.666
0.176199	27.147	154.073	214.131
0.191334	28.160	147.177	209.168
0.21867	31.852	145.663	212.283
0.246679	37.938	153.794	226.301
0.352398	54.295	154.0733	243.121
0.422878	64.476	152.4479	251.260

Λ_o[1] vs. c intercept: 172.621
Slope: 195.383
Corr.: 0.9810
172.621 - 73.7= 98.92

See end of table for footnotes.

APPENDIX II (Continued)

NaOH, 25°C

Concentration[a]	Conductivity[b]	Λ	Λ_o[1]
0.08484	19.426	228.972	263.9
0.10425	24.07	230.887	270.0
0.13032	30.67	235.344	279.9
0.15638	36.67	234.493	283.6
0.18244	43.67	239.366	293.4
0.2121	51.626	243.404	302.6
0.22869	54.49	238.270	299.4
0.28587	68.39	239.235	308.7
0.29694	73.026	245.928	317.9

Λ_o[1] vs. c intercept: 247.3
Slope: 234.332
Corr.: 0.9815
247.3 - 50.1 = 197.2

NaOH, 35°C

Concentration[a]	Conductivity[b]	Λ	Λ_o[1]
0.10425	25.825	247.718	294.3
0.13032	32.047	245.913	298.4
0.15638	39.731	254.065	312.9
0.18244	47.540	260.584	325.4
0.22869	60.177	263.138	337.0
0.28587	75.861	265.369	349.5
0.34304	91.736	267.419	361.1
0.40022	106.848	266.973	369.5
0.45739	131.485	287.469	402.2

Λ_o[1] vs. c intercept: 267.7
Slope: 279.9
Corr.: 0.9864
267.7 - 61.5 = 206.2

See end of table for footnotes.

APPENDIX II (Continued)

NaOH, 45°C

Concentration[a]	Conductivity[b]	Λ	Λ_o[1]
0.10425	28.686	275.165	330.3
0.13934	38.658	277.445	342.2
0.15638	43.955	281.078	350.5
0.17417	48.624	279.174	352.6
0.18244	52.903	289.975	366.6
0.20900	59.414	284.272	366.2
0.22869	68.986	301.657	390.1
0.24384	71.854	294.679	385.5
0.27867	80.170	287.685	384.6
0.28587	87.134	304.803	405.7
0.34304	104.906	305.813	418.1
0.40022	130.788	326.790	453.4
0.45739	148.898	325.538	462.3

Λ_o[1] vs. c intercept: 290.3
Slope: 385.237
Corr.: 0.9865
290.3 - 73.7 = 216.6

Na_2IDA, 25°C

Ionic Strength[a]	Conductivity[b]	Λ	Λ_o[1]
0.208749	10.05	48.144	84.21
0.260934	12.86	49.284	90.32
0.313122	15.34	49.990	94.47
0.36537	18.51	50.661	100.63
0.417495	21.51	51.522	105.68
0.500169	27.81	55.601	116.64
0.625212	35.01	55.997	125.91
0.750252	41.01	54.662	132.56
0.875295	47.81	54.622	140.44
1.00034	54.71	54.691	148.20

Λ_o[1] vs. c intercept: 70.75
Slope: 81.167
Corr.: 0.991
70.75 - 50.1 = 20.65

See end of table for footnotes.

APPENDIX II (Continued)

Na_2IDA, 35°C

Ionic Strength[a]	Conductivity[b]	Λ	Λ_o[1]
0.208749	12.5044	59.902	105.68
0.260934	15.5686	59.665	111.55
0.313122	19.1543	61.172	118.99
0.36537	22.1533	60.6325	123.76
0.417495	24.2390	58.0582	125.86
0.500169	32.7150	65.4079	142.35
0.625212	42.038	67.238	155.74
0.750252	49.339	65.763	164.49
0.875295	57.554	65.7538	174.61
1.00034	66.029	66.0067	184.76

Λ_o[1] vs. c intercept: 86.659
Slope: 101.792
Corr.: 0.994
86.659 - 61.5 = 25.16

Na_2IDA, 45°C

Ionic Strength[a]	Conductivity[b]	Λ	Λ_o[1]
0.208749	14.912	71.437	127.23
0.206934	18.232	69.872	132.95
0.313122	22.853	72.986	143.50
0.36537	26.694	73.060	150.20
0.417495	30.534	73.137	156.58
0.500169	39.777	79.527	173.77
0.625212	50.192	80.279	188.413
0.750252	58.003	77.311	197.69
0.875295	68.417	78.165	211.21
1.00034	78.767	78.740	224.04

Λ_o[1] vs. c intercept: 107.06
Slope: 120.66
Corr.: 0.994
107.60 - 73.7 = 33.36

See end of table for footnotes.

APPENDIX II (Continued)

$KHCO_3$, 25°C

Concentration[a]	Conductivity[b,c]	Λ	Λ_o[1]
0.15175	20.741	102.060	137.535
0.18969	24.997	104.085	144.430
0.22763	29.715	107.464	152.540
0.24898	30.001	102.418	149.179
0.26557	33.785	107.437	156.600
0.30351	38.041	108.029	161.158
0.31123	36.814	103.824	157.111
0.37347	44.053	105.904	165.433
0.43572	51.170	107.108	172.462
0.49796	58.348	108.135	179.060

Λ_o[1] vs. c intercept: 123.33
Slope: 113.87
Corr.: 0.982
123.33 - 73.50 = 49.83

$KHCO_3$, 35°C

Concentration[a]	Conductivity[b,c]	Λ	Λ_o[1]
0.15175	23.531	117.796	161.968
0.18969	28.431	120.110	170.351
0.22763	34.863	128.313	184.986
0.24898	35.762	124.066	183.118
0.26557	40.075	129.609	191.624
0.30351	44.377	127.581	194.212
0.31123	44.335	126.798	194.280
0.37347	53.280	129.617	205.087
0.43572	62.039	131.201	214.114
0.49796	70.736	132.268	222.251

Λ_o[1] vs. c intercept: 141.9
Slope: 167.408
Corr.: 0.983
141.9 - 88.22 = 53.68

See end of table for footnotes.

APPENDIX II (Continued)

$KHCO_3$, 45°C

Concentration[a]	Conductivity[b,c]	Λ	Λ_o[1]
0.15175	27.308	139.318	193.021
0.18969	33.538	144.297	205.656
0.22763	41.265	154.193	223.437
0.31123	54.926	159.508	243.099
0.37347	65.452	161.108	254.317
0.43572	74.963	159.919	261.774
0.49796	85.362	160.814	271.310

Λ_o[1] vs. c intercept: 166.66
Slope: 222.18
Corr.: 0.979
166.66 - 103.4 = 63.26

Na_2CO_3, 25°C

Ionic Strength[a]	Conductivity[b]	pH	Λ	Λ_o[1]
0.19247	29.093	9.56	85.650	124.279
0.23946	34.546	9.61	85.194	128.783
0.28482	40.301	9.66	85.770	133.933
0.32478	46.359	9.72	86.632	138.678
0.39620	72.96	10.02	92.381	151.734
0.45693	87.16	10.12	90.579	154.788
0.55074	100.06	10.17	88.429	159.761
0.62709	113.76	10.23	87.377	164.313
0.73722	96.733	9.99	85.187	169.647

Λ_o[1] vs. I intercept: 110.852
Slope: 86.161
Corr.: 0.974
110.852-50.1 = 60.75

See end of table for footnotes.

APPENDIX II (Continued)

Na_2CO_3, 35°C

Ionic Strength[a]	Conductivity[b]	pH	Λ	Λ_o[1]
0.20868	36.322	9.49	117.356	170.016
0.25275	43.243	9.56	116.089	174.581
0.302516	50.419	9.60	116.279	181.113
0.32952	59.309	9.76	113.124	180.739
0.34510	58.674	9.66	119.307	189.742
0.35775	60.261	9.72	112.277	183.054
0.403398	67.818	9.74	115.958	192.524
0.445785	76.136	9.82	114.045	194.906
0.44714	79.629	9.87	114.607	195.718
0.52957	84.963	9.78	116.872	207.081
0.53449	91.694	9.90	114.652	204.906
0.60286	102.044	9.92	116.441	213.937
0.73318	116.776	9.94	113.654	222.988
0.75014	121.031	9.97	113.711	224.637
0.8076	141.605	10.04	123.356	242.137

Λ_o[1] vs. c intercept: 147.178
Slope: 109.271
Corr.: 0.9887
147.178 - 61.5 = 85.68

Na_2CO_3, 45°C

Ionic Strength[a]	Conductivity[b]	pH	Λ	Λ_o[1]
0.25044	42.631	9.23	141.252	212.584
0.30450	50.393	9.28	138.757	218.146
0.35631	58.844	9.34	138.914	225.898
0.40149	68.735	9.43	142.557	236.498
0.41154	70.425	9.48	139.772	234.589
0.46893	79.439	9.52	139.234	241.594
0.52455	90.019	9.60	139.185	248.671
0.55281	95.089	9.59	141.942	255.565
0.58527	99.972	9.62	140.381	257.679
0.63567	108.110	9.66	139.350	262.517
0.70545	119.629	9.69	139.914	271.462
0.80949	146.797	9.79	148.800	294.721
0.86169	151.805	9.75	148.288	300.016
0.93834	166.829	9.82	147.708	307.857

Λ_o[1] vs. c intercept: 176.067
Slope: 141.275
Corr.: 0.9968
176.067 - 73.7 = 102.37

[a]Concentration and ionic strength units: equiv/1 x 10^6.
[b]Conductivity units: micromhos.
[c]Includes conductivity due to NaOH, not identical in all samples.

APPENDIX III

DATA FROM WHICH IMINODIACETIC ACID DISSOCIATION CONSTANTS WERE CALCULATED

Temperature, °C	Acid Concentration, M C_A	Moles Base / Moles Acid, a	pH	$k_2 \times 10^{10}$
25	8.610×10^{-4}	1.501	9.670	1.723
		1.528	9.708	1.731
		1.626	9.846	1.704
		1.737	9.982	1.745
		1.893	10.171	1.742
25	7.002×10^{-4}	1.397	9.525	1.601
		1.537	9.733	1.573
		1.568	9.771	1.587
		1.628	9.862	1.512
		1.737	9.986	1.541
		1.828	10.091	1.518
35	1.110×10^{-3}	1.353	9.203	3.208
		1.389	9.275	3.145
		1.426	9.316	3.319
		1.463	9.382	3.277
		1.507	9.440	3.381
35	1.053×10^{-3}	1.306	9.131	3.068
		1.375	9.261	3.053
		1.445	9.365	3.163
		1.509	9.462	3.204
		1.574	9.555	3.270
45	2.774×10^{-3}	1.420	9.263	3.847
		1.482	9.374	3.799
		1.554	9.485	3.888
		1.641	9.611	4.102
		1.693	9.705	4.093
45	8.325×10^{-4}	1.355	9.087	4.222
		1.432	9.228	4.139
		1.547	9.380	4.484
		1.614	9.468	4.676

APPENDIX IV

DATA FROM WHICH STABILITY CONSTANTS FOR THE CALCIUM-IMINODIACETIC ACID COMPLEX WERE CALCULATED

Temperature, °C	Acid Concentration, C_A (moles/L)	Calcium Concentration, C_M (moles/L)	Mole Base / Mole Acid, a	pH	Stability Constant K x 10^{-3}
25	1.140×10^{-3}	8.002×10^{-4}	1.403	9.171	3.035
			1.490	9.331	3.157
25	1.438×10^{-3}	8.730×10^{-4}	1.391	9.204	2.323
			1.460	9.328	2.478
			1.530	9.456	2.519
			1.599	9.566	2.830
			1.669	9.687	3.022
25	5.695×10^{-4}	1.092×10^{-3}	1.500	9.159	3.099
			1.594	9.305	3.235
35	9.286×10^{-4}	9.797×10^{-4}	1.566	9.190	2.107
			1.676	9.363	2.434
			1.725	9.445	2.589
35	7.784×10^{-4}	9.865×10^{-4}	1.601	9.208	2.333
			1.662	9.307	2.454
			1.729	9.410	2.730
45	9.977×10^{-4}	9.992×10^{-4}	1.201	8.364	1.791
			1.403	8.847	1.583
			1.604	9.184	1.852
45	1.070×10^{-3}	1.049×10^{-3}	1.349	8.74	1.601
			1.432	8.92	1.460
			1.618	9.23	1.696
			1.660	9.30	1.777
			1.708	9.38	1.910

APPENDIX V

COMPLEX DISSOCIATION DATA

IDA = 0.4527M
t = 0 when addition of 10 mL 6.085 x 10^{-4}M Na_2EDTA was complete
Reported values are raw conductivity readings x 10^{-4}

COMPLEX DISSOCIATION, 25°C

Time, seconds	IDA = 0 mL	IDA = 5 mL	IDA = 10 mL	IDA = 15 mL
0	2.92	2.50	2.19	1.769
30	2.75	2.37	2.08	1.677
60	2.75	2.37	2.07	1.676
120	2.75	2.37	2.07	1.675
300	2.74	2.36	2.07	1.672
600	2.72	2.35	2.06	1.668
1000	2.71	2.35	2.06	1.663
1250	2.70	2.34	2.05	1.660
1500	2.69	2.34	2.05	1.656

COMPLEX DISSOCIATION, 35°C

Time, seconds	IDA = 0 mL	IDA = 5 mL	IDA = 10 mL	IDA = 15 mL
0	2.87	2.56	2.21	1.800
15	2.73	2.43	2.10	1.708
30	2.73	2.43	2.10	1.708
60	2.73	2.43	2.10	1.707
120	2.73	2.42	2.10	1.706
300	2.73	2.42	2.10	1.705
600	2.73	2.41	2.10	1.702
1000	2.72	2.40	2.09	1.695
1500	2.71	2.39	2.08	1.694

COMPLEX DISSOCIATION, 45°C

Time, seconds	IDA = 0 mL	IDA = 5 mL	IDA = 10 mL	IDA = 15 mL
0	3.64	3.22	2.80	2.41
15	3.46	3.05	2.65	2.29
30	3.46	3.06	2.66	2.28
60	3.46	3.05	2.66	2.28
300	3.47	3.05	2.66	2.28
600	3.46	3.05	2.66	2.28
1000	3.45	3.04	2.65	2.28
1500	3.44	3.03	2.64	2.27

APPENDIX VI

THE COMPUTER PROGRAM FOR CALCULATING CALCIUM AND CARBONATE CONCENTRATIONS FROM EXPERIMENTAL DATA

A computer program was written, in the FORTRAN language, to convert experimental conductivity and pH data into calcium and carbonate concentrations. The calculations, described on page 46 in the Experimental Section, involve straightforward mass and charge balances, the Onsager equation for calculating equivalent conductances, and the definitions of the complex stability constant and the acid dissociation constant.

Temperature affects the carbonate-bicarbonate equilibrium constant; the IDA dissociation constant, Y; the Ca-IDA complex stability constant, X; the dissociation constant of water; and the solubility product of calcium carbonate, SPK. Temperature also alters all of the equivalent conductance calculations. The equations affected by temperature are underlined in the following programs, each used for a specific temperature. Note that the carbonate-bicarbonate equilibrium constant is changed numerically in the calculation of ALPHA and the dissociation constant of water is similarly changed in the calculation of OHCA. (A complete listing of the symbols used follows the programs.)

APPENDIX VI (Continued)

At 25°C, the following program was used.

```
C         THIS PROGRAM CALCULATES CALCIUM AND
C         CARBONATE CONCENTRATIONS FROM EXPERIMENTAL DATA
          WRITE(6,4)
4          FORMAT(1H ,'TIME',2X,'CONDUCTIVITY',2X,'PH',5X,'CALCIUM',6X,
     1    'CARBONATE',2X,'ITERATIONS',2X,'CA*CO3-KSP/F2**2',2X,'TEMP')
7          READ(5,1)M,SOD,PH,C,DAI,VI,B,T
 1         FORMAT(I2,F8.5,F5.2,F10.8,F8.5,F8.5,F8.5,I5)
          IF(M+1)8,8,9
9         CAC=0.00
          N=1
         SI=SOD+VI
5         F1=10.**(-.5*(SI**0.5/(1.0+SI**0.5)-0.3*SI))
          F2=10.**(-1.*(SI**0.5/(1.0+SI**0.5)-0.3*SI))
         A=1.0*EXP(2.303*(-1.0*PH))
          ALPHA=A*F2/F1/(4.69*EXP(2.303*(-11.)))
          ECOH=256.7-185.121*SI**0.5
          ECSOD=125.14-89.420*SI**0.5
          ECCO3=120.25-231.90*SI**0.5
          ECHCO3=109.33-137.852*SI**0.5
          Y=1.66*EXP(2.303*(-10.0))
          R=Y/A
         DAI1=DAI/(R+1.)
          DA2T=R*DAI1
          X=2951.2
          IF(N-1)11,11,12
11        CA=0.00050
          GO TO 12
12       DAI2=DA2T/((CA*X)+1.)
          DACA=DAI-DAI1-DAI2
         V=VI+B-DAI1-2*DA2T-SOD
         OHCA=1.0*EXP(2.303*(-14.))/A-V
          ECV=247.3-117.514*SI**0.5
          ECDAI1=70.75-76.911*SI**0.5
          ECDAI2=70.75-117.65*SI**0.5
          CO3=(1000.*C-ECOH*OHCA-ECSOD*SOD-ECDAI1*DAI1-ECDAI2*DAI2-
     2    ECV*V)/(2.*ECCO3+ALPHA*ECHCO3)
          HCO3=ALPHA/2.*CO3
          SI=SOD+4.*CO3+3.*HCO3+3.*OHCA+V+DAI1+3.*DAI2
         CA=CO3+HCO3+OHCA
          IF((CA-CAC)/CA-0.01)3,3,2
2         CAC=CA
          N=N+1
          GO TO 5
3          SPK=4.55*EXP(2.303*(-9.0))
         Z=(CA*CO3)-(SPK/(F2**2))
           WRITE(6,6)M,C,PH,CA,CO3,N,Z,T
6          FORMAT(1H ,I2,2H ,E12.4,2H ,F5.2,2H ,E11.3,2H ,E11.3,2H ,I2,
     0     2H ,E11.3,2H ,I5)
          WRITE(6,10)F2
10        FORMAT(1H ,'F2=',F10.5)
          GO TO 7
8         CALL EXIT
          END
```

APPENDIX VI (Continued)

At 35°C, the temperature-dependent variables were changed, resulting in the following program.

```
C          THIS PROGRAM CALCULATES CALCIUM AND
C          CARBONATE CONCENTRATIONS FROM EXPERIMENTAL DATA
           WRITE(6,4)
4           FORMAT(1H ,'TIME',2X,'CONDUCTIVITY',2X,'PH',5X,'CALCIUM',6X,
     1     'CARBONATE',2X,'ITERATIONS',2X,'CA*CO3-KSP/F2**2',2X,'TEMP')
7          READ(5,1)M,SOD,PH,C,DAI,VI,B,T
 1         FORMAT(I2,F8.5,F5.2,F10.8,F8.5,F8.5,F8.5,I5)
           IF(M+1)8,8,9
9          CAC=0.00
           N=1
          SI=SOD+VI
5          F1=10.**(-.5*(SI**0.5/(1.0+SI**0.5)-0.3*SI))
           F2=10.**(-1.*(SI**0.5/(1.0+SI**0.5)-0.3*SI))
          A=1.0*EXP(2.303*(-1.0*PH))
          ALPHA=A*F2/F1/(5.58*EXP(2.303*(-11.)))
           ECOH=279.4-219.241*SI**0.5
          ECSOD=146.98-109.989*SI**0.5
          ECCO3=158.88-300.047*SI**0.5
          ECHCO3=126.88-169.791*SI**0.5
          Y=3.39*EXP(2.303*(-10.0))
           R=Y/A
          DAI1=DAI/(R+1.)
           DA2T=R*DAI1
          X=2398.8
           IF(N-1)11,11,12
11         CA=0.00050
           GO TO 12
12        DAI2=DA2T/((CA*X)+1.)
           DACA=DAI-DAI1-DAI2
          V=VI+B-DAI1-2*DA2T-SOD
          OHCA=2.09*EXP(2.303*(-14.0))/A-V
          ECV=267.7-138.288*SI**0.5
          ECDAI1=86.66-95.849*SI**0.5
          ECDAI2=86.66-146.600*SI**0.5
           CO3=(1000.*C-ECOH*OHCA-ECSOD*SOD-ECDAI1*DAI1-ECDAI2*DAI2-
     2     ECV*V)/(2.*ECCO3+ALPHA*ECHCO3)
           HCO3=ALPHA/2.*CO3
           SI=SOD+4.*CO3+3.*HCO3+3.*OHCA+V+DAI1+3.*DAI2
          CA=CO3+HCO3+OHCA
           IF((CA-CAC)/CA-0.01)3,3,2
2          CAC=CA
           N=N+1
           GO TO 5
3         SPK=3.545*EXP(2.303*(-9.0))
          Z=(CA*CO3)-(SPK/(F2**2))
            WRITE(6,6)M,C,PH,CA,CO3,N,Z,T
6           FORMAT(1H ,I2,2H ,E12.4,2H ,F5.2,2H ,E11.3,2H ,E11.3,2H ,I2,
     0      2H ,E11.3,2H ,I5)
           WRITE(6,10)F2
10         FORMAT(1H ,'F2=',F10.5)
           GO TO 7
8          CALL EXIT
           END
```

APPENDIX VI (Continued)

At 45°C, the program used was as follows.

```
C         THIS PROGRAM CALCULATES CALCIUM AND
C         CARBONATE CONCENTRATIONS FROM EXPERIMENTAL DATA
          WRITE(6,4)
4          FORMAT(1H ,'TIME',2X,'CONDUCTIVITY',2X,'PH',5X,'CALCIUM',6X,
     1    'CARBONATE',2X,'ITERATIONS',2X,'CA*CO3-KSP/F2**2',2X,'TEMP')
7          READ(5,1)M,SOD,PH,C,DAI,VI,B,T
 1         FORMAT(I2,F8.5,F5.2,F10.8,F8.5,F8.5,F8.5,I5)
          IF(M+1)8,8,9
9          CAC=0.00
          N=1
         SI=SOD+VI
5          F1=10.**(-.5*(SI**0.5/(1.0+SI**0.5)-0.3*SI))
          F2=10.**(-1.*(SI**0.5/(1.0+SI**0.5)-0.3*SI))
        A=1.0*EXP(2.303*(-1.0*PH))
        ALPHA=A*F2/F1/(6.38*EXP(2.303*(-11.)))
        ECOH=304.8-257.195*SI**0.5
        ECSOD=172.62-133.106*SI**0.5
        ECCO3=190.57-366.006*SI**0.5
        ECHCO3=151.46-206.736*SI**0.5
        Y=4.17*EXP(2.303*(-10.0))
         R=Y/A
        DAI1=DAI/(R+1.)
         DA2T=R*DAI1
        X=1717.9
         IF(N-1)11,11,12
11       CA=0.00050
         GO TO 12
12      DAI2=DA2T/((CA*X)+1.)
         DACA=DAI-DAI1-DAI2
        V=VI+B-DAI1-2*DA2T-SOD
        OHCA=4.02*EXP(2.303*(-14.0))/A-V
        ECV=290.3-161.266*SI**0.5
        ECDAI1=107.06-119.062*SI**0.5
        ECDAI2=107.06-180.117*SI**0.5
         CO3=(1000.*C-ECOH*OHCA-ECSOD*SOD-ECDAI1*DAI1-ECDAI2*DAI2-
     2   ECV*V)/(2.*ECCO3+ALPHA*ECHCO3)
         HCO3=ALPHA/2.*CO3
         SI=SOD+4.*CO3+3.*HCO3+3.*OHCA+V+DAI1+3.*DAI2
        CA=CO3+HCO3+OHCA
         IF((CA-CAC)/CA-0.01)3,3,2
2        CAC=CA
         N=N+1
         GO TO 5
3       SPK=2.715*EXP(2.303*(-9.0))
        Z=(CA*CO3)-(SPK/(F2**2))
          WRITE(6,6)M,C,PH,CA,CO3,N,Z,T
6          FORMAT(1H ,I2,2H ,E12.4,2H ,F5.2,2H ,E11.3,2H ,E11.3,2H ,I2,
     0     2H ,E11.3,2H ,I5)
         WRITE(6,10)F2
10       FORMAT(1H ,'F2=',F10.5)
         GO TO 7
8        CALL EXIT
         END
```

APPENDIX VI (Continued)

The symbols used in the preceding programs are summarized in the following table.

COMPUTER PROGRAM SYMBOLS

A = (H^+)

ALPHA = (H^+) F2 $(F1)^{-1}$ (carbonate-bicarbonate equilibrium constant)$^{-1}$

B = Sodium content in Na_2CO_3

C = Conductivity

CA = (Ca^{++})

CAC = (Ca^{++})

CO_3 = $(Ca^{++}\ CO_3^{=})$

DAI = Total iminodiacetic acid

DAI1 = $(HIDA^-)$

DA2T = Total $(IDA^=)$

DAI2 = Free $(IDA^=)$

DACA = (Ca-IDA complex)

ECCO3 = Λ for $CaCO_3$

ECDAI1 = Λ for NaHIDA

ECDAI2 = Λ for Na_2IDA

ECHCO3 = Λ for $Ca(HCO_3)_2$

ECOH = Λ for $Ca(OH)_2$

ECSOD = Λ for $NaNO_3$

ECV = Λ for NaOH

F1 = Monovalent activity coefficient

F2 = Divalent activity coefficient

HCO3 = $(Ca(HCO_3)_2)$

APPENDIX VI (Continued)

COMPUTER PROGRAM SYMBOLS (Continued)

M = Minutes

N = Iterations

OHCA = $(Ca(OH)_2)$

PH = pH

R = $(IDA^{=})/(HIDA^{-})$

SI = Ionic strength

SOD = $(NaNO_3)$

SPK = K_{sp} for $CaCO_3$

T = Temperature

V = (NaOH)

VI = NaOH added

X = Complex stability constant

Y = Second acid dissociation constant of IDA

Z = $(Ca^{++})(CO_3^{=}) - K_{sp}/f_2^2$

APPENDIX VII

CALCITE GROWTH DATA

/DATA

TIME	CONDUCTIVITY	PH	CALCIUM	CARBONATE	ITERATIONS		
1 ,	0.3714E-03 ,	10.88 ,	0.643E-03 ,	0.464E-03 ,	3 ,	0.292E-06 ,	25
F2=	0.86936						
3 ,	0.3685E-03 ,	10.88 ,	0.627E-03 ,	0.450E-03 ,	3 ,	0.276E-06 ,	25
F2=	0.86999						
5 ,	0.3665E-03 ,	10.88 ,	0.616E-03 ,	0.440E-03 ,	3 ,	0.265E-06 ,	25
F2=	0.87043						
8 ,	0.3645E-03 ,	10.87 ,	0.607E-03 ,	0.447E-03 ,	3 ,	0.265E-06 ,	25
F2=	0.87058						
10 ,	0.3634E-03 ,	10.87 ,	0.601E-03 ,	0.442E-03 ,	3 ,	0.259E-06 ,	25
F2=	0.87082						
15 ,	0.3610E-03 ,	10.87 ,	0.587E-03 ,	0.430E-03 ,	3 ,	0.247E-06 ,	25
F2=	0.87134						
20 ,	0.3592E-03 ,	10.86 ,	0.579E-03 ,	0.438E-03 ,	3 ,	0.248E-06 ,	25
F2=	0.87145						
25 ,	0.3576E-03 ,	10.86 ,	0.570E-03 ,	0.430E-03 ,	3 ,	0.239E-06 ,	25
F2=	0.87180						
1 ,	0.3658E-03 ,	10.71 ,	0.631E-03 ,	0.657E-03 ,	3 ,	0.409E-06 ,	25
F2=	0.86693						
3 ,	0.3626E-03 ,	10.71 ,	0.614E-03 ,	0.642E-03 ,	3 ,	0.388E-06 ,	25
F2=	0.86761						
5 ,	0.3606E-03 ,	10.71 ,	0.603E-03 ,	0.633E-03 ,	3 ,	0.375E-06 ,	25
F2=	0.86803						
8 ,	0.3584E-03 ,	10.70 ,	0.591E-03 ,	0.632E-03 ,	3 ,	0.367E-06 ,	25
F2=	0.86836						
10 ,	0.3571E-03 ,	10.70 ,	0.583E-03 ,	0.626E-03 ,	3 ,	0.359E-06 ,	25
F2=	0.86863						
12 ,	0.3560E-03 ,	10.70 ,	0.577E-03 ,	0.621E-03 ,	3 ,	0.352E-06 ,	25
F2=	0.86887						
15 ,	0.3545E-03 ,	10.69 ,	0.569E-03 ,	0.622E-03 ,	3 ,	0.348E-06 ,	25
F2=	0.86905						
20 ,	0.3523E-03 ,	10.69 ,	0.557E-03 ,	0.612E-03 ,	3 ,	0.335E-06 ,	25
F2=	0.86952						
25 ,	0.3502E-03 ,	10.68 ,	0.545E-03 ,	0.611E-03 ,	3 ,	0.327E-06 ,	25
F2=	0.86983						
1 ,	0.4094E-03 ,	10.76 ,	0.843E-03 ,	0.808E-03 ,	3 ,	0.675E-06 ,	25
F2=	0.85887						
3 ,	0.4056E-03 ,	10.76 ,	0.822E-03 ,	0.790E-03 ,	3 ,	0.644E-06 ,	25
F2=	0.85965						
5 ,	0.4035E-03 ,	10.75 ,	0.811E-03 ,	0.791E-03 ,	3 ,	0.636E-06 ,	25
F2=	0.85992						
8 ,	0.4014E-03 ,	10.75 ,	0.800E-03 ,	0.781E-03 ,	3 ,	0.619E-06 ,	25
F2=	0.86035						
12 ,	0.3993E-03 ,	10.75 ,	0.788E-03 ,	0.771E-03 ,	3 ,	0.602E-06 ,	25
F2=	0.86079						
15 ,	0.3979E-03 ,	10.74 ,	0.781E-03 ,	0.775E-03 ,	3 ,	0.599E-06 ,	25
F2=	0.86092						
20 ,	0.3959E-03 ,	10.74 ,	0.770E-03 ,	0.765E-03 ,	3 ,	0.583E-06 ,	25
F2=	0.86133						
25 ,	0.3940E-03 ,	10.73 ,	0.760E-03 ,	0.766E-03 ,	3 ,	0.576E-06 ,	25
F2=	0.86157						

CA*CO3-KSP/F2**2 TEMP

APPENDIX VII (Continued)

/DATA

TIME	CONDUCTIVITY	PH	CALCIUM	CARBONATE	ITERATIONS		
1 ,	0.4658E-03	,10.68 ,	0.786E-03 ,	0.353E-03	, 3 ,	0.273E-06 ,	350
F2=	0.86542						
3 ,	0.4624E-03	,10.68 ,	0.772E-03 ,	0.341E-03	, 3 ,	0.259E-06 ,	35
F2=	0.86598						
5 ,	0.4602E-03	,10.67 ,	0.762E-03 ,	0.351E-03	, 3 ,	0.263E-06 ,	35
F2=	0.86614						
8 ,	0.4577E-03	,10.67 ,	0.751E-03 ,	0.342E-03	, 3 ,	0.252E-06 ,	35
F2=	0.86654						
10 ,	0.4563E-03	,10.67 ,	0.746E-03 ,	0.337E-03	, 3 ,	0.247E-06 ,	35
F2=	0.86677						
15 ,	0.4534E-03	,10.66 ,	0.732E-03 ,	0.344E-03	, 3 ,	0.247E-06 ,	35
F2=	0.86706						
20 ,	0.4510E-03	,10.66 ,	0.722E-03 ,	0.336E-03	, 3 ,	0.238E-06 ,	35
F2=	0.86745						
25 ,	0.4487E-03	,10.65 ,	0.711E-03 ,	0.345E-03	, 3 ,	0.240E-06 ,	35
F2=	0.86764						
1 ,	0.4480E-03	,10.50 ,	0.688E-03 ,	0.535E-03	, 3 ,	0.363E-06 ,	35
F2=	0.86572						
3 ,	0.4440E-03	,10.50 ,	0.671E-03 ,	0.522E-03	, 3 ,	0.345E-06 ,	35
F2=	0.86636						
5 ,	0.4416E-03	,10.50 ,	0.660E-03 ,	0.514E-03	, 3 ,	0.335E-06 ,	35
F2=	0.86674						
8 ,	0.4392E-03	,10.49 ,	0.649E-03 ,	0.515E-03	, 3 ,	0.329E-06 ,	35
F2=	0.86703						
10 ,	0.4379E-03	,10.49 ,	0.643E-03 ,	0.511E-03	, 3 ,	0.324E-06 ,	35
F2=	0.86724						
13 ,	0.4362E-03	,10.48 ,	0.634E-03 ,	0.514E-03	, 3 ,	0.321E-06 ,	35
F2=	0.86742						
15 ,	0.4352E-03	,10.48 ,	0.630E-03 ,	0.511E-03	, 3 ,	0.317E-06 ,	35
F2=	0.86758						
20 ,	0.4330E-03	,10.47 ,	0.619E-03 ,	0.512E-03	, 3 ,	0.312E-06 ,	35
F2=	0.86785						
25 ,	0.4309E-03	,10.46 ,	0.609E-03 ,	0.513E-03	, 3 ,	0.308E-06 ,	35
F2=	0.86811						
1 ,	0.4966E-03	,10.54 ,	0.809E-03 ,	0.654E-03	, 3 ,	0.524E-06 ,	35
F2=	0.85982						
3 ,	0.4916E-03	,10.54 ,	0.788E-03 ,	0.637E-03	, 3 ,	0.497E-06 ,	35
F2=	0.86060						
5 ,	0.4890E-03	,10.53 ,	0.776E-03 ,	0.638E-03	, 3 ,	0.490E-06 ,	35
F2=	0.86089						
8 ,	0.4862E-03	,10.53 ,	0.764E-03 ,	0.629E-03	, 3 ,	0.476E-06 ,	35
F2=	0.86133						
10 ,	0.4846E-03	,10.53 ,	0.757E-03 ,	0.623E-03	, 3 ,	0.467E-06 ,	35
F2=	0.86158						
12 ,	0.4832E-03	,10.53 ,	0.751E-03 ,	0.619E-03	, 3 ,	0.460E-06 ,	35
F2=	0.86179						
15 ,	0.4813E-03	,10.52 ,	0.742E-03 ,	0.622E-03	, 3 ,	0.457E-06 ,	35
F2=	0.86199						
20 ,	0.4785E-03	,10.52 ,	0.730E-03 ,	0.613E-03	, 3 ,	0.442E-06 ,	35
F2=	0.86242						
25 ,	0.4758E-03	,10.51 ,	0.717E-03 ,	0.613E-03	, 3 ,	0.435E-06 ,	35
F2=	0.86275						

CA*CO3-KSP/F2**2 TEMP

APPENDIX VII (Continued)

```
/DATA
TIME     CONDUCTIVITY  PH      CALCIUM       CARBONATE  ITERATIONS
 2 ,     0.7942E-03 ,10.59 ,   0.894E-03 ,   0.658E-03 , 3 , 0.584E-06 ,   45
F2=      0.84796
 5 ,     0.7868E-03 ,10.58 ,   0.863E-03 ,   0.660E-03 , 3 , 0.566E-06 ,   45
F2=      0.84867
 8 ,     0.7828E-03 ,10.58 ,   0.848E-03 ,   0.648E-03 , 3 , 0.546E-06 ,   45
F2=      0.84913
10 ,     0.7810E-03 ,10.58 ,   0.842E-03 ,   0.643E-03 , 3 , 0.537E-06 ,   45
F2=      0.84935
15 ,     0.7780E-03 ,10.57 ,   0.827E-03 ,   0.658E-03 , 3 , 0.540E-06 ,   45
F2=      0.84954
20 ,     0.7762E-03 ,10.57 ,   0.820E-03 ,   0.652E-03 , 3 , 0.531E-06 ,   45
F2=      0.84975
25 ,     0.7750E-03 ,10.56 ,   0.811E-03 ,   0.672E-03 , 3 , 0.541E-06 ,   45
F2=      0.84975
 1 ,     0.7460E-03 ,10.60 ,   0.750E-03 ,   0.489E-03 , 3 , 0.362E-06 ,   45
F2=      0.85367
 2 ,     0.7420E-03 ,10.60 ,   0.735E-03 ,   0.476E-03 , 3 , 0.346E-06 ,   45
F2=      0.85415
 4 ,     0.7370E-03 ,10.60 ,   0.717E-03 ,   0.461E-03 , 3 , 0.327E-06 ,   45
F2=      0.85475
 5 ,     0.7350E-03 ,10.60 ,   0.710E-03 ,   0.455E-03 , 3 , 0.319E-06 ,   45
F2=      0.85499
 8 ,     0.7308E-03 ,10.60 ,   0.695E-03 ,   0.442E-03 , 3 , 0.303E-06 ,   45
F2=      0.85550
10 ,     0.7288E-03 ,10.59 ,   0.683E-03 ,   0.462E-03 , 3 , 0.312E-06 ,   45
F2=      0.85556
12 ,     0.7268E-03 ,10.59 ,   0.675E-03 ,   0.456E-03 , 3 , 0.304E-06 ,   45
F2=      0.85580
15 ,     0.7246E-03 ,10.59 ,   0.668E-03 ,   0.449E-03 , 3 , 0.296E-06 ,   45
F2=      0.85607
20 ,     0.7216E-03 ,10.58 ,   0.652E-03 ,   0.465E-03 , 3 , 0.300E-06 ,   45
F2=      0.85626
25 ,     0.7190E-03 ,10.58 ,   0.642E-03 ,   0.457E-03 , 3 , 0.290E-06 ,   45
F2=      0.85657
                                                  CA*CO3-KSP/F2**2  TEMP
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